Marine Ecosystem Uptake of Nuclear Reprocessing Derived Radiocarbon (^{14}C)

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Submitted in fulfilment of the requirements for the
Degree of Doctor of Philosophy

Scottish Universities Environmental Research Centre

University of Glasgow

July 2017

Acknowledgements

I would like to thank my supervisors, Professor Gordon Cook, Dr Sheila Heymans, Dr Gillian MacKinnon, Dr John Howe, Dr Sheng Xu and, also, Professor Gus Mackenzie for their advice and guidance throughout this project. My thanks to Dr Graham Muir for his support at every stage of the work presented here including his assistance on fieldwork ("jollies"), which rarely involved a dull moment.

A number of people collaborated and helped on various aspects of this project and without them the nature of this work would have been hugely limited. They include staff at the Scottish Universities Environmental Research Centre Radiocarbon and AMS laboratories, the Scottish Association for Marine Science, the Scottish Marine Animal Stranding Scheme, the UK Cetacean Stranding Investigation Programme, the Ecopath International Consortium, Marine Scotland Science, the Agri-Food and Biosciences Institute and the crews of RV Prince Madog and RV Calanus.

Thank you to RATE and Lo-RISE consortia members for their thoughts and input on this work. I want to thank my fellow RATE and SUERC PhD candidates for their support and especially to Helen, Daisy, Helena, Pete and Dimitris for the craic.

I would like to acknowledge the Natural Environment Research Council, the Environment Agency and Radioactive Waste Management Ltd who funded the project (grant number NE/L000202/1).

Finally, I am hugely grateful for the help and encouragement from my friends and family on every step of this path, despite them not believing that this was a "real job".

Declaration

Chapters contained in this thesis have either been published (Chapters 2, 3 and 4), are in press (Chapter 5) or been submitted for publication (Chapter 6) in various peer-reviewed journals at the date of the thesis being submitted. Kieran M. Tierney is the lead author on four of these articles and is the second author on the other (Chapter 3). Reference to each article and co-authors are given at the beginning of each chapter.

This thesis has not been submitted for any other degree at the University of Glasgow or any other institution.

Kieran M. Tierney

Abstract

The nuclear energy industry produces radioactive waste at various stages of the fuel cycle. In the United Kingdom, spent fuel is reprocessed at the Sellafield facility (formerly known as Windscale), in Cumbria on the north-west coast of England. Waste generated at the site comprises a wide range of radionuclides, including radiocarbon (^{14}C) which, due to its long half-life (5730 years), environmental mobility and high bio-availability, is the largest contributor to collective dose commitment from the entire nuclear industry. ^{14}C is disposed of in various forms, one of which is as highly soluble inorganic carbon within the low-level liquid radioactive effluent, *via* pipelines, into the Irish Sea. The discharged ^{14}C is then rapidly incorporated into the dissolved inorganic carbon (DIC) pool.

This project aimed to better understand the fate of Sellafield discharges of ^{14}C to the marine environment. Investigations of intertidal sites in the Irish Sea and West of Scotland found ^{14}C enrichment above ambient background levels in shell material, including at the most northerly site, located 265 km north of Sellafield. Dissolved inorganic ^{14}C is readily utilised during shell formation by calcifying organisms and mussel shell ^{14}C activities at sites closer to Sellafield appear to be varying in response to the total Sellafield ^{14}C discharge activity over the preceding 5 years. Due to subsequent erosion of this material, ^{14}C is transferred to finer fractions of intertidal sediments where it is accumulating.

During photosynthesis, primary producing organisms also utilise carbon derived from the DIC pool. This uptake and the trophic-level transfer of ^{14}C within the Irish Sea and West of Scotland marine environments were examined. The ^{14}C activities of Irish Sea DIC and biota in the east and west basins were enriched and highly variable. A general decrease in ^{14}C activity with distance from Sellafield was observed, although, enriched activities were also found in the West of Scotland where the activities were more homogenous. Organic sediments were significantly less enhanced than associated benthic organisms. This could be due to rapid scavenging of labile, ^{14}C-enriched organic material by organisms and mixing to depth with older, ^{14}C depleted material. Commercially important species were ^{14}C enriched; however, the radiation dose from their consumption is extremely low and radiologically insignificant.

To evaluate the transfer of ^{14}C to top predators in the UK marine environment, ^{14}C activities were examined in stranded marine mammals. All Irish Sea samples were enriched, as were most from the West of Scotland, although the ^{14}C activities were lower. In demonstrating transfer of enriched ^{14}C to apex predators for the first time, this study also showed that marine mammal activities correlated significantly with distance from Sellafield and Sellafield ^{14}C discharge activities for 24 months prior to stranding. These measurements also provided some insight into harbour porpoise (*Phocoena phocoena*) ecology, indicating high foraging fidelity and suggesting the animals stranded on the West of Scotland did not forage in the Irish Sea.

The studies in this thesis examined the dispersion of Sellafield-derived ^{14}C to both near- and far-field sites and the subsequent ecosystem uptake and trophic transfer at these locations. However, it is important to attempt to understand the fate of ^{14}C discharges beyond the limitations and scope of analytical investigations. To do so, the first spatial-temporal ecosystem model to predict the ecological fate of Sellafield-derived ^{14}C was developed. The observed trends in ^{14}C activities between different species were predicted by the model which illustrated the integration of ^{14}C in species at higher trophic levels through time.

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Chapter 1
Project Background

This chapter provides a summarised overview and background information relevant to all studies described in this thesis and the overarching project aims. Thereafter, Chapters 2-6 each contain an introductory section specific to the study presented in that chapter.

1.1 ^{14}C Natural Production

Radiocarbon (^{14}C) is a naturally occurring radionuclide with a relatively long half-life of 5730 ± 40 years (Godwin, 1962) and is a weak beta emitter (E_{max} = 156 keV), decaying to stable ^{14}N. ^{14}C is produced in the upper atmosphere by the bombardment of atmospheric nitrogen atoms (^{14}N) with cosmic-ray produced neutrons. The neutrons are thermalised by successive collisions and become available for capture by atmospheric nitrogen atoms, forming ^{14}C with the release of a proton (Libby, 1946; Cook *et al*., 2009) *via* the following reaction:

$$^{14}N(n,p)^{14}C$$

The rate of natural production is not constant due to centennial and millennial scale fluctuations and is, therefore, difficult to calculate (Bronk Ramsey *et al*., 2007), although, production estimations of between 0.92 x 10^{15} Becquerels (Bq) $year^{-1}$ and 1.5 x 10^{15} Bq $year^{-1}$ have been made (Bush *et al*., 1983; UNSCEAR 2000). Short scale variation is considered a result of sun-spot activity (Stuiver 1961; Baxter and Walton 1971; Damon *et al*., 1973) whereas changes in the earth's magnetic dipole moment cause changes in the cosmic ray flux which produces long scale variation (Elsasser *et al*., 1956; Mazaud *et al*., 1991). Newly produced ^{14}C is initially incorporated as carbon monoxide (^{14}CO) but enters the global carbon cycle after further oxidation to carbon dioxide ($^{14}CO_2$; Pandow *et al*., 1960; MacKay *et al*., 1963). Carbon fixation during photosynthesis results in the uptake of ^{14}C into primary producing organisms and is subsequently transferred to all living organisms. In the environment, ^{14}C is present in very low concentrations in comparison to the stable carbon isotopes where $^{12}C \approx 98.9\%$, $^{13}C \approx 1.1\%$ and $^{14}C \approx 1$ atom per 7×10^{11} stable atoms of carbon (Beer *et al*., 2012).

1.2 The Suess Effect and Bomb Peak

The onset of the industrial revolution introduced the "Suess Effect" whereby combustion of fossil fuels which, because of their great age, are essentially free from measurable ^{14}C, caused large scale releases of stable carbon to the environment as $^{12/13}CO_2$ and diluted the activity of $^{14}CO_2$ (Suess, 1955). This led to a reduction in atmospheric ^{14}C concentrations up to 1950 (Stuiver and Quay, 1981), and between 1850 and 1950 atmospheric ^{14}C concentrations had an apparent reduction of 2-3% (Oeschger *et al*., 1975). In the early 1950s, the Suess Effect was offset by the production of ^{14}C by nuclear weapons testing. Similar to natural production of ^{14}C, thermal neutrons produced by an atmospheric nuclear explosion are readily captured by atmospheric ^{14}N producing significant amounts of artificial or 'bomb' ^{14}C. The newly produced ^{14}C atoms, released from the nuclear detonation, are rapidly oxidised to $^{14}CO_2$ by the explosion (MacKay *et al*., 1963). The increasing number of atmospheric weapons tests between the 1950s and early 1960s caused an increase in atmospheric ^{14}C activity resulting in a recorded northern hemisphere maximum in 1964 of almost double the natural specific activity (Nydal and Lovseth, 1965). In 1963, the former Soviet Union, the UK and USA signed a partial atmospheric test ban treaty, resulting in significantly fewer subsequent atmospheric tests (Carter and Moghissi, 1977). Atmospheric ^{14}C concentrations have subsequently declined due to atmosphere-ocean CO_2 exchange and uptake into the terrestrial biosphere.

1.3 ^{14}C Production in the Nuclear Fuel Cycle

^{14}C is the largest contributor to total collective dose from the entire nuclear industry (UNSCEAR, 2016). Production of ^{14}C occurs in nuclear reactors through neutron activation of ^{13}C, ^{14}N and ^{17}O, which are present in the fuel, cladding, moderator, coolant and structural materials (Davis, 1977). ^{14}C production depends on the reactor type which is normally classified by their coolant type. Graphite-moderated reactors such as Magnox reactors and Advanced Gas-cooled Reactors (AGRs), which have produced most of the nuclear power in the UK, produce relatively high volumes of ^{14}C compared to other reactor types (IAEA, 2004). Magnox and AGR ^{14}C production has been estimated at 13.99 and 8.025 TBq ^{14}C per gigawatt of electricity produced per year (GWe-a), respectively (Bush *et al*., 1984). Of the total ^{14}C produced, the World Health Organization (1983) estimated Magnox reactors released 3% and AGRs 6%, during

normal operations. Although, in 2010, AGRs discharged an estimated 1.4 TBq ^{14}C to the atmosphere and 0.2 TBq ^{14}C to aqueous routes per GW produced (UNSCEAR, 2016); approximately 20% of the estimated annual production. Graphite moderated reactor discharges of ^{14}C are typically a consequence of ^{14}C produced in the coolant while the reactor is running but also occur on reactor-shut-downs or gas purging operations.

Most of the ^{14}C produced during reactor operations is retained in fuel and structural materials. The UK derived ^{14}C inventory for 2013 was 17,700 TBq, an increase from 9820 TBq in 2010, which is mainly due to the inclusion of waste and spent fuel projected for the UK's nuclear new build programme (NDA, 2016). Of this inventory, 18.6% (3290 TBq) is from spent fuel, which is significant in environmental terms as reprocessing of spent fuel materials at Sellafield provides the largest single source of liquid ^{14}C discharges to the UK marine environment. During reprocessing, the shearing of fuel rods releases ^{14}C trapped in the inner rod gas space to the off-gases (Bush *et al*., 1984; IAEA, 2004). The sheared fuel is treated with nitric acid under oxidising conditions and most of the ^{14}C within the fuel is liberated as $^{14}CO_2$ into the off-gases, with a comparatively insignificant amount left in solution (IAEA 2004). Discharges of ^{14}C arise from releases of off-gases directly to the atmosphere and from liquid discharges after scrubbing out of ^{14}C from off-gases.

1.4 Sellafield Discharges

The Sellafield nuclear fuel reprocessing plant (formerly known as Windscale) is authorised to discharge low level radioactive waste, including ^{14}C, to the environment. Discharges can occur either to the atmosphere in gaseous form (predominantly as $^{14}CO_2$) or as dissolved inorganic carbon (DIC) in liquid effluent (likely to be in the form of dissolved carbonate $^{14}CO_3^{2-}$ and bicarbonate - $H^{14}CO_3^-$) which is released into the marine environment (Begg *et al*., 1992; Cook *et al*., 1995). The Sellafield reprocessing plant is located on the north-west coast of England and discharges of low level waste (LLW) to the marine environment are made via pipelines which extend 2.1 km offshore into the Irish Sea.

Nuclear fuel reprocessing and discharges of radioactive waste at Sellafield began in 1952. Since the 1970s new facilities have been introduced to improve effluent treatment and reduce the amount of activation and fission products released to the marine environment.

During this period, Sellafield began treating fuel storage pond water with zeolite, which uptakes radionuclides including ^{137}Cs and ^{90}Sr, and a new flocculation-precipitation plant for actinides was introduced. Discharges of medium active liquors to the Irish Sea ceased in 1980. The Site Ion Exchange Effluent Plant (SIXEP) began operations in 1985 treating contaminated water by filtration through natural zeolite clay, clinoptilolite, which has a very high cation exchange capacity and ability to reduce the concentrations of caesium radionuclides and ^{90}Sr present in liquid effluent. The Salt Evaporator also came online in 1985 and removed effluent salts produced during reprocessing that contain high levels of alpha and beta emitting radionuclides. In 1994, the Segregated Effluent Treatment Plant (SETP) and Enhanced Actinide Reprocessing Plant (EARP) commenced operations. SETP aids storage of low level radioactive effluent prior to analysis and discharge and EARP further reduces discharges of actinides such as ^{241}Am and plutonium isotopes through a ferric oxide scavenging process. Subsequently, marine discharges of a number of radionuclides, including ^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu, of which discharges were historically high, have since substantially decreased (Figure 1.1). This is despite an increase in the quantity of fuel reprocessed at Sellafield, particularly since the introduction of the Thermal Oxide Reprocessing Plant (THORP) in 1994 which allowed reprocessing of fuel from AGR and light water reactors.

In contrast, the increase in reprocessing activities in 1994 resulted in an increase in ^{14}C discharges and, due to a change in policy to scrub out gaseous ^{14}C, marine discharges of ^{14}C have increased significantly (Figure 1.1). Discharges of ^{14}C from Sellafield have occurred since 1952 when reprocessing began, although monitoring of ^{14}C discharges only began in 1984 (BNFL, 1985). Estimates of ^{14}C marine discharges between 1966 and 1984 range between 0.85 and 8.52 TBq year^{-1}, although are typically less than 4 TBq (Cook *et al*., 2004a). Between 1984 and 1993, Sellafield discharged, on average, 1.78 TBq year^{-1} of ^{14}C to the Irish Sea (BNFL, 1985-1989; MAFF, 1992-1995). The changes in 1994 resulted in an increase in marine ^{14}C discharges to 8.17 TBq for that year and relatively high discharge activities have occurred since, reaching an annual peak of 17 TBq in 2003 with an average of 7.63 TBq year^{-1} released between 1994 and 2015 (MAFF, 1994, 1995; RIFE, 1996-2016). In comparison, atmospheric ^{14}C discharges declined in 1995 and an average of 0.93 TBq year^{-1} was released between 1995 and 2015. Marine discharges of ^{14}C to the Irish Sea are significant as they are the dominant contributor to the total collective dose for UK, European and global populations from Sellafield radionuclide releases (NDA, 2015). The total collective dose is the sum of all of the

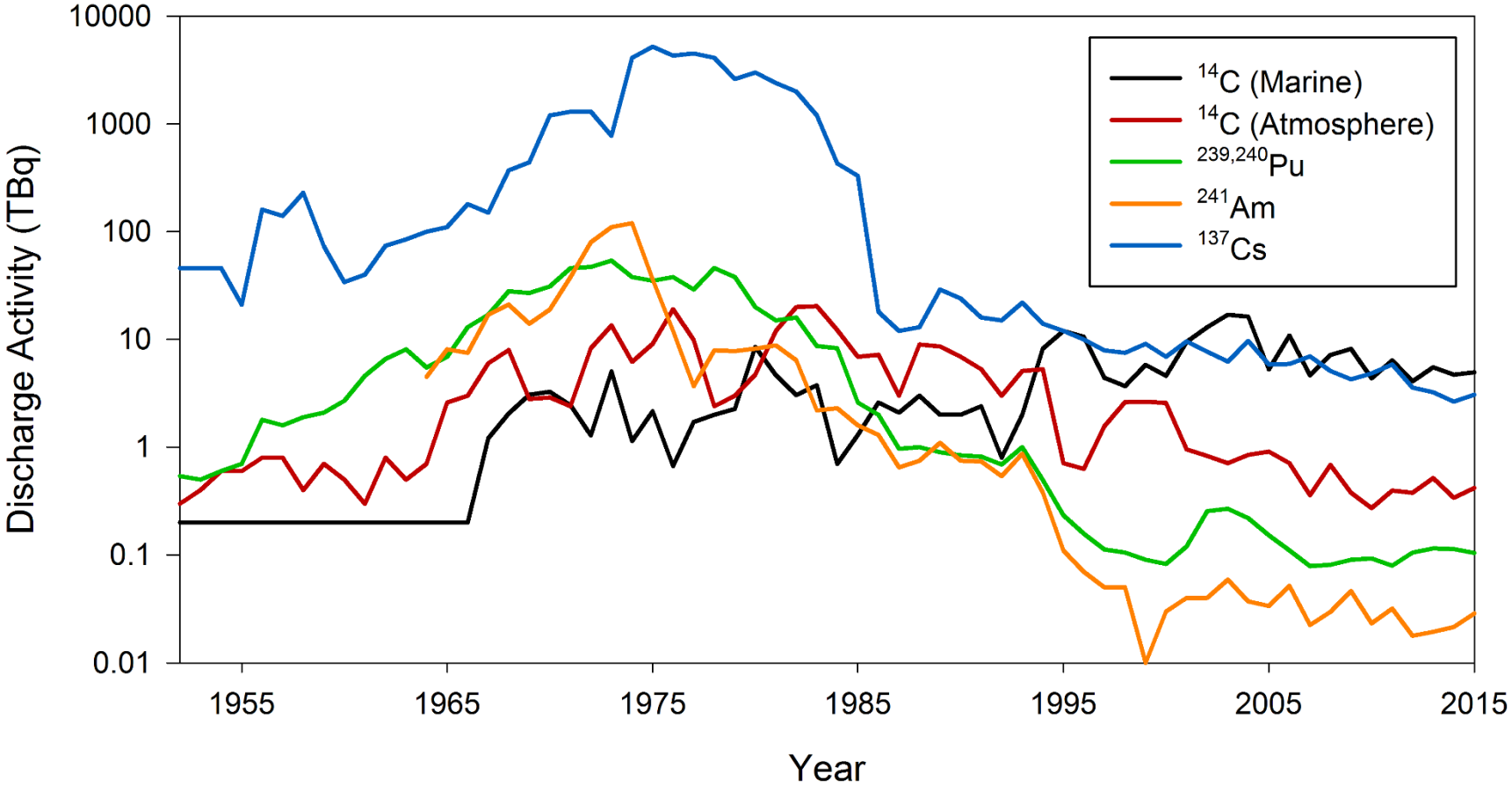

Figure 1.1 Sellafield marine discharge activities for ^{14}C, $^{239,240}Pu$, ^{241}Am and ^{137}Cs and atmospheric discharge activities for ^{14}C. Note that measurements for ^{241}Am discharges could only be obtained from 1964 and marine ^{14}C discharge activities between 1952 and 1967 were assumed to be 0.2 TBq year^{-1}.

doses to members of a population. Although the individual dose of ^{14}C may be small, due to its long half-life and high bioavailability, nuclear reprocessing-derived ^{14}C is transferred throughout the biosphere and, therefore, the total collective dose is relatively high.

1.5 Sellafield-Derived ^{14}C in the Marine Environment

1.5.1 ^{14}C Marine Background

To indicate ^{14}C enrichment in the environment, a background ^{14}C activity must be defined. As Sellafield ^{14}C discharges are made in addition to existing inputs of ^{14}C from natural production and fallout from atmospheric testing of nuclear weapons, this background activity must come from contemporary samples which exhibit modern ^{14}C activities in marine systems. Cook *et al*. (1998) aimed to address the lack of information regarding a UK marine background for ^{14}C in 1995. From measurements of marine samples from a site remote from UK ^{14}C discharges, Burton Port on the west coast of Ireland, they presented a background ^{14}C activity of 248 ± 1.0 Bq kg^{-1} C. The marine environment in this area is strongly influenced by Atlantic water so should be free of any ^{14}C input from Sellafield. This background value is indicative of the regional ^{14}C background for marine surface waters. Water masses with little or no gaseous exchange with the atmosphere, for example deeper oceanic water, will typically exhibit a more depleted ^{14}C activity as there is little input of contemporary ^{14}C and the ^{14}C within the water mass will decay through time.

1.5.2 Dispersion of Sellafield ^{14}C

Sellafield ^{14}C discharges to the Irish Sea are incorporated into the DIC component of seawater. Dispersion of ^{14}C is, therefore, controlled by local and regional circulation patterns. The Irish Sea is semi-enclosed and connected to the North Atlantic via the St. Georges Channel to the south, and the North Channel to the north. The net northerly movement of water dictates the long-term dilution and dispersion of Sellafield marine discharges (Dunster, 1998) and Sellafield ^{14}C is largely dispersed in solution through the North Channel (Gulliver *et al*., 2001). Variable transit times of 3 months to 1.8 years from Sellafield to the North Channel have been estimated for the highly soluble caesium isotopes, ^{134}Cs and ^{137}Cs, (Jefferies *et al*., 1973; Kershaw and Baxter, 1995) and for ^{99}Tc

(Kershaw *et al*., 2004). Transit times for ^{14}C in the DIC reservoir would be of a similar order to these conservative radionuclides. The variability in transit time may result from seasonal variability in flow direction in the Irish Sea and North Channel which is occasionally reversed (Dabrowski *et al*., 2008, 2010). Flow direction in the North Channel can change over periods of days and is influenced by high winds and storms (Brown and Gmitrowicz, 1995). A southerly flow of water from the Atlantic also exists in the western North Channel; however, the southwards flux is low relative to the northwards flux (Brown and Gmitrowicz, 1995). Irish Sea water moving through the North Channel becomes a significant component of the Scottish Coastal Current (McKay *et al*., 1986; Hill and Simpson, 1988). This, in turn, is a source of water to the Fair Isle Current which flows around the northern Scottish coast and into the North Sea (Turrell and Henderson, 1990), carrying Sellafield-derived ^{14}C with it (Gulliver *et al*., 2004).

The known dispersion routes for Sellafield discharges mean that in addition to investigating sites proximate to Sellafield in the eastern Irish Sea, such as the mud-patch as discussed below, it is also important to consider sites further afield when assessing the fate of Sellafield-derived ^{14}C. Although dissolved ^{14}C will likely be dispersed throughout the Irish Sea, the prevailing northward currents mean that the North Channel is a region of significant importance for the longer-term transport of Sellafield-derived ^{14}C out of the Irish Sea (Gulliver *et al*., 2001). This could make areas in the West of Scotland important sinks when assessing the long-term fate of Sellafield-derived ^{14}C.

1.5.3 Sellafield Mud-Patch

A number of radionuclides derived from Sellafield marine discharges, including ^{137}Cs, ^{241}Am, ^{238}Pu and $^{239,240}Pu$, are strongly associated with a deposit of silt and mud in the eastern Irish Sea that is commonly referred to as the "Sellafield mud-patch" (Pentreath *et al*., 1984; MacKenzie *et al*., 1987, 1998, 1999, 2000; Kershaw *et al*., 1992; McCartney *et al*., 1994; Cook *et al*., 1997; Hunt *et al*., 1985). Input of Sellafield-derived ^{14}C to mud-patch inorganic and, in particular, organic sediment fractions have also been identified (Cook *et al*., 1995; Wolstenholme *et al*., 1998; Wolstenholme 1999; Gulliver 2002). However, incorporation of ^{14}C into the mud-patch sediments has appeared to be minimal and Gulliver (2002) estimated that the mud-patch ^{14}C inventory only accounted for between 0.08 and 1.2 % of the total ^{14}C discharges up to 1998.

1.5.4 ^{14}C Uptake by Calcifying Organisms

Marine calcifying organisms such as mollusc species predominantly utilise DIC as a carbon source for building their calcium carbonate shell. Analyses of inorganic carbon in intertidal sediments, and whole shells (Cook *et al*., 2004b) revealed enriched ^{14}C activities in whole shell and to a lesser extent, in coarse sediment (>500µm) fractions, at sites north of Sellafield, of up to 2000 Bq kg^{-1} C. A decade later, increases in ^{14}C activities at the same sites were found, including up to 2600 Bq kg^{-1} C in mussel shells (Muir *et al*., 2015). The erosion of enriched shells gradually increases the inorganic ^{14}C activity in intertidal sediments and is apparent from enriched ^{14}C activities in coarse (>500 um) and finer (<63 – 500um) sediments fractions (Muir *et al*., 2015). This process of ^{14}C uptake through calcification and subsequent erosion will also add ^{14}C to the particulate inorganic carbon (PIC) pool in the marine environment (Figure 1.2). Redissolution of this material could provide a secondary source of ^{14}C to the DIC pool.

1.5.5 ^{14}C Uptake by Photosynthesis

In the marine environment, DIC is the primary carbon source for photosynthesising organisms. As a result, marine primary producers will incorporate and transfer ^{14}C to the particulate organic carbon (POC) and, subsequently, the dissolved organic carbon (DOC) pools (Figure 1.2; Cook *et al*., 1995; Wolstenholme *et al*., 1999). In addition, ^{14}C enters the food web and is subject to trophic transfer to other organisms. Enriched ^{14}C activities have been found in marine and intertidal species in the UK environment (Begg *et al*., 1992; Cook *et al*., 1995, 1998, 2004b). ^{14}C enrichment in intertidal species (mollusc and seaweed) sampled at the low-water mark demonstrated that these organisms were deriving their carbon predominantly from marine DIC enriched in ^{14}C. Conversely, primary producers (seaweed) sampled at the high-water mark and, therefore, exposed to the atmosphere for longer periods, were found to utilise atmospheric CO_2 and had lower ambient ^{14}C activities (Cook *et al*., 2004b). Activities as high as 2600 Bq kg^{-1} C in seaweed, 4400 Bq kg^{-1} C in mussels and 2700 Bq kg^{-1} C in flatfish species were found in the Sellafield area in 1995 but enriched activities were also observed at sites further afield including the west of Scotland marine environment (Cook *et al*., 1998). Sellafield is also considered to be the source of enriched ^{14}C activities measured in seaweed and mussels at sites in the east of Scotland (Gulliver *et al*., 2004), demonstrating the long-distance dispersion to sites around the Scottish coastline.

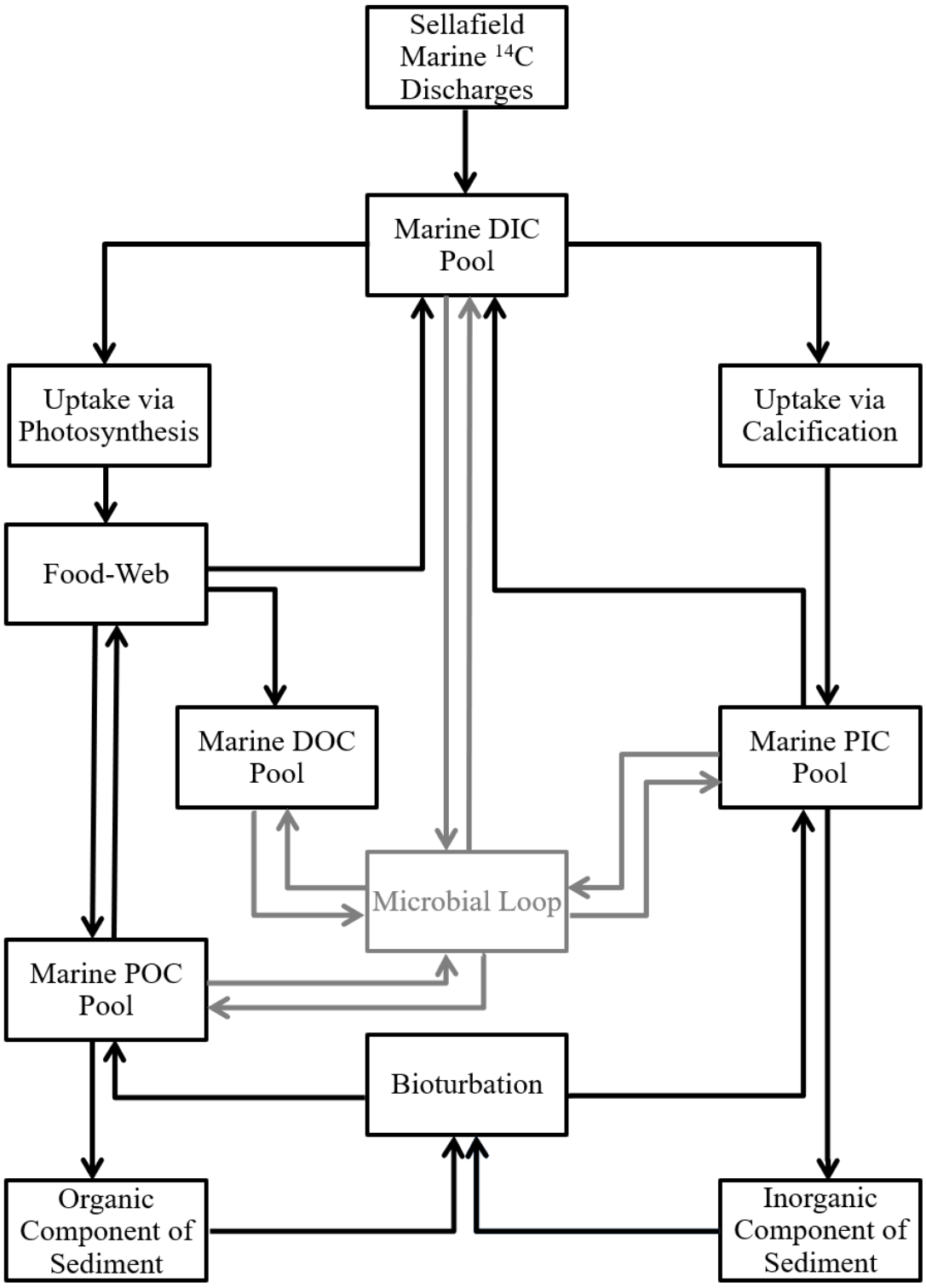

Figure 1.2 Conceptual model of ecological transfer pathways for ^{14}C in the marine environment. The microbial loop was not part of this project; however, it is shown to indicate the possible role of microbes in transferring ^{14}C between the various carbon pools. The photosynthesising and calcifying uptake pathways were investigated during this project as were the subsequent transfer of ^{14}C to different carbon pools and the sediments.

1.6 Project Aims

This project was undertaken as part of the NERC Radioactivity and the Environment (RATE) programme. A central objective of RATE was to improve knowledge on transfer pathways for radionuclides in terrestrial and aquatic systems, including chemical speciation and its impact on environmental pathways. Within RATE, this project was part of the Long-lived radionuclides in the surface environment (Lo-RISE) consortium which sought to improve our understanding of environmentally mobile radionuclides that are readily taken up by organisms, using field, laboratory and modelling approaches.

Due to its long half-life and continued discharge from Sellafield, significant questions remain unanswered on the fate of nuclear reprocessing-derived ^{14}C in the UK environment. Additionally, ^{14}C is important when considering the fate of potential releases from long-term radioactive waste disposal systems, i.e. a nuclear waste repository. Within the marine realm, discharged ^{14}C is incorporated in living organisms and is easily transported to areas far from source, making it important to further investigate the fate of ^{14}C in this environment. To this purpose, the specific aims of this PhD research were to:

1) Determine the contemporary UK ^{14}C marine background to identify any ^{14}C enrichment as a result of Sellafield activities.
2) Develop a mechanistic understanding of uptake, transport and accumulation of ^{14}C in the inorganic component of intertidal sediments on the British west coast, addressing both particle and solution transport of inorganic ^{14}C.
3) Examine the transfer and extent of ^{14}C incorporation into near-source biotic and abiotic ecosystem components of the Irish Sea.
4) Examine ^{14}C transport to sites remote from Sellafield (West of Scotland) and the extent of ^{14}C incorporation into biotic and abiotic ecosystem components.
5) Investigate the trophic transfer of ^{14}C in the marine food web in relation to spatial and temporal changes in ambient ^{14}C activity. Spatial variation is explored to an extent in Chapters 3 and 4 and spatial-temporal changes are investigated in detail in Chapter 5.
6) Model the ecosystem uptake and trophic transfer of ^{14}C in the UK marine environment.

During the course of this research, five articles have been produced, 3 of which have been published in international, peer-reviewed journals; 1 publication is ‘in press’ (July

2017) and a further manuscript has been submitted for publication (June 2017). Each article is presented in the following chapters in turn. Chapter 2 investigates aims 1 and 2 and describes the UK ^{14}C marine background and the ^{14}C activities in the inorganic fraction of intertidal sediments, including whole shells, at sites near to and distant from Sellafield. Contemporary ^{14}C activities of biotic and abiotic ecosystem components in the Irish Sea (aim 3) and West of Scotland (aim 4) marine environments are presented in Chapters 3 and 4 respectively. These include discussions of ^{14}C uptake and transfer through the marine ecosystems from phytoplankton to benthic species and activities present in different marine carbon pools and organic sediments sampled during this research. The transfer of ^{14}C to top predators in the marine environment is described in Chapter 5, where archives of marine mammal tissues from stranded animals were utilised to identify changes in ^{14}C trophic transfer, both spatially and temporally to address aim 5. Chapter 6 was motivated by aim 6 and is a modelling study on the spatial and temporal ecosystem uptake and trophic transfer of Sellafield-derived ^{14}C.

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Chapter 2

Accumulation of Sellafield-derived Radiocarbon (^{14}C) in Irish Sea and West of Scotland Intertidal Shells and Sediments

Abstract

The nuclear energy industry produces radioactive waste at various stages of the fuel cycle. In the United Kingdom, spent fuel is reprocessed at the Sellafield facility in Cumbria on the north-west coast of England. Waste generated at the site comprises a wide range of radionuclides including radiocarbon (^{14}C) which is disposed of in various forms including highly soluble inorganic carbon within the low-level liquid radioactive effluent, via pipelines into the Irish Sea. This ^{14}C is rapidly incorporated into the dissolved inorganic carbon (DIC) reservoir and marine calcifying organisms, e.g. molluscs, readily utilise DIC for shell formation. This study investigated a number of sites located in Irish Sea and West of Scotland intertidal zones. Results indicate ^{14}C enrichment above ambient background levels in shell material at least as far as Port Appin, 265 km north of Sellafield. Of the commonly found species (blue mussel (*Mytilus edulis*), common cockle (*Cerastoderma edule*) and common periwinkle (*Littorina littorea*), mussels were found to be the most highly enriched in ^{14}C due to the surface environment they inhabit and their feeding behaviour. Whole mussel shell activities appear to have been decreasing in response to reduced discharge activities since the early 2000s but in contrast, there is evidence of continuing enrichment of the carbonate sediment component due to in-situ shell erosion, as well as indications of particle transport of fine ^{14}C-enriched material close to Sellafield.

This chapter has been published as:

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2.1 Introduction

The Sellafield nuclear fuel reprocessing plant (formerly known as Windscale), located in Cumbria on the north-west coast of England (Figure 2.1), is the primary source of anthropogenic radiocarbon (^{14}C) discharges to the UK environment. The ^{14}C waste that arises during fuel reprocessing is discharged under authorisation to the atmosphere and the Irish Sea (Figure 2.2). Discharges of low-level liquid radioactive effluent, containing ^{14}C, are via pipelines that extend 2.1 km offshore, while regulated discharges to the atmosphere are made from a wide range of facilities at the site, including the fuel storage ponds, reprocessing plants and waste treatment plants (RIFE 2011). Reprocessing of radioactive waste has been ongoing since 1952, however, monitoring of ^{14}C discharges only began in 1984 (BNFL 1985). Subsequently, discharges for the earlier period to both the atmosphere and the north-east Irish Sea were estimated by measuring the ^{14}C activity in annual rings from trees felled in close proximity to Sellafield (Gray *et al.*, 1995; McNamara and McCartney 1998; Isogai *et al.*, 2002) and annually collected seaweed (Cook *et al.*, 2004a), respectively. Between 1984 and 1993 Sellafield discharged, on average, 1.78 TBq year^{-1} of ^{14}C to the Irish Sea (BNFL 1985-1989; MAFF 1992-1994). However, an increase in the volume of waste reprocessed and, to a larger extent, a change in discharge policy in 1994 resulted in an increase in aquatic ^{14}C discharges to 8.17 TBq for that year. ^{14}C discharges peaked in 2003 and although discharged activities have since reduced, they have remained relatively high. On average, Sellafield has discharged 8.13 TBq year^{-1} between 1994 and 2013 (MAFF 1995; RIFE 1996-2014). Its long half-life (5730 years), high environmental mobility and high bio-availability make Sellafield-derived ^{14}C the largest contributor to the collective dose commitment to UK and European populations from the entire nuclear industry (BNFL 2002). Also, ^{14}C is estimated to be the largest contributor to the collective total dose that the global population receives from nuclear fuel processes (UNSCEAR 2008). Therefore, it is very important to understand its distribution and long-term fate in the environment.

^{14}C is discharged into the Irish Sea primarily as inorganic carbon and is incorporated into the dissolved inorganic carbon (DIC) component of seawater (Begg *et al.*, 1992). Enhanced ^{14}C activities in the DIC component of seawater have previously been detected at a range of sites around the British coastline (Cook *et al.*, 1998). Marine mollusc species predominantly utilise DIC for shell formation (McConnaughey *et al.*, 1997) and so

Figure 2.1. UK map (a) with study area (b) showing Sellafield and study sites.

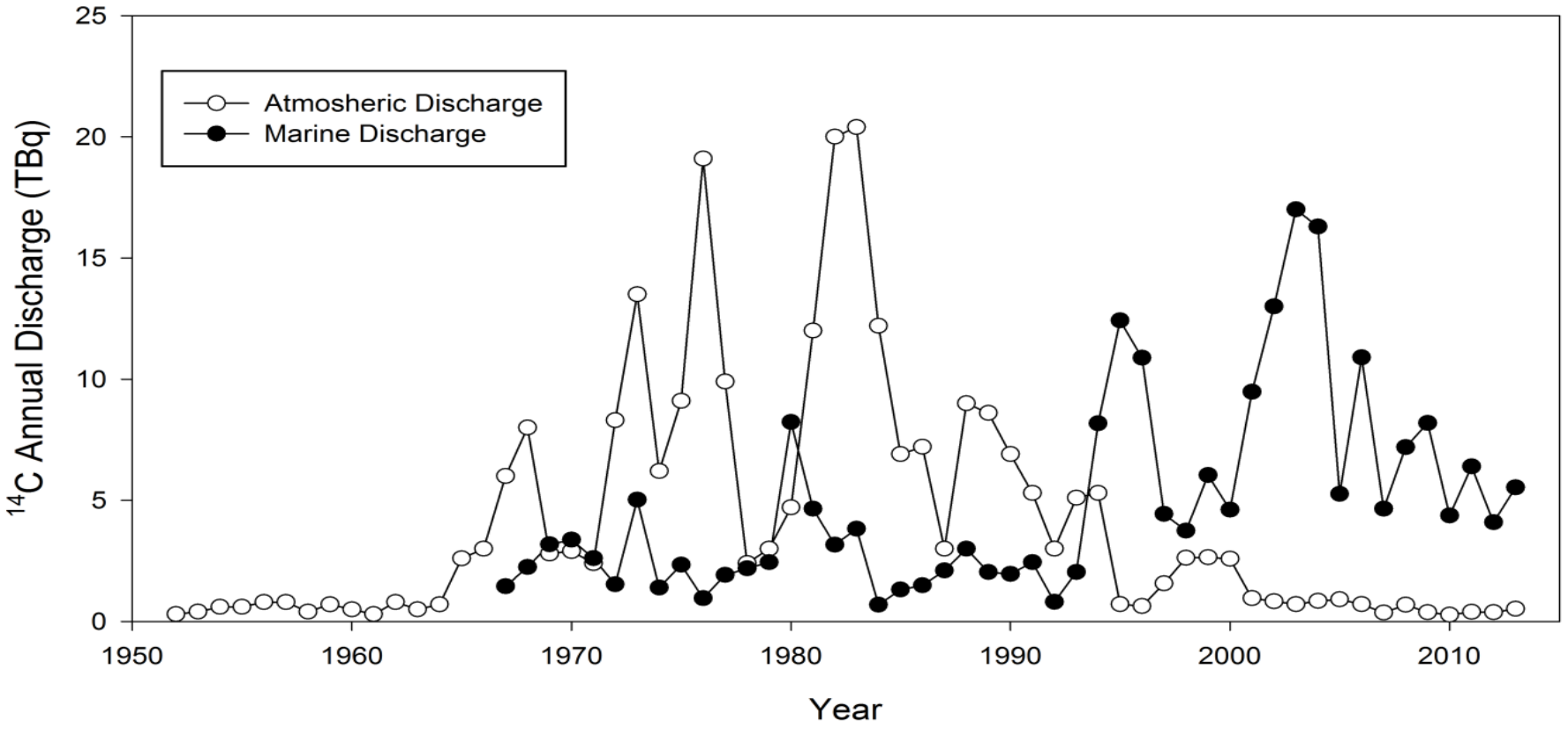

Figure 2.2. Sellafield atmospheric and marine annual ^{14}C discharges (TBq). Data prior to 1995 for atmospheric discharges (Isogai *et al.*, 2002) and prior to 1985 for marine discharges (Cook *et al.*, 2004a) are estimated. The subsequent measured data were taken from BNFL (1985-1989), MAFF (1992-1995) and RIFE (1996-2014) reports.

have the potential to incorporate ^{14}C during calcification. Analysis of shells and sedimentary inorganic carbon by Cook *et al.* (2004b) revealed enhanced activities in whole shell and, to a lesser extent, in coarse sediment (>500 µm) fractions at near-field sites to the north of Sellafield, with a trend of decreasing activity with increasing distance from Sellafield. Following this study, Muir *et al.* (2015) found shell and sediment ^{14}C activities had increased at the same sites between 2001 and 2011. It was also confirmed that as ^{14}C-enriched shells erode they contribute ^{14}C to the sediment, gradually increasing the activity of progressively finer sediments within the intertidal zone (Muir *et al.,* 2015). These two studies were confined to an area where transport of Sellafield-derived radionuclides is largely dominated by particle transport (Mackenzie *et al.,* 1987), which has been suggested as a possible mechanism for redistributing fine material enriched in ^{14}C (Muir *et al.,* 2015).

Long-term dilution and dispersion of Sellafield aquatic discharges are dictated by a net northerly movement of water through the North Channel and wind driven turbulent diffusion (Dunster 1998). Water moving through the North Channel becomes a significant component of the Scottish Coastal Current (McKay *et al.,* 1986; Hill and Simpson 1988) and this, in turn, is a contributory source of water to the Fair Isle Current that flows round the northern Scottish coast and into the North Sea (Turrell and Henderson 1990). Despite its high bioavailability, close to 100% of ^{14}C discharged from Sellafield is dispersed northwards through the North Channel (Wolstenholme *et al.,* 1998; Gulliver *et al.,* 2001) and is subsequently transported in solution around the Scottish coastline (Gulliver *et al.,* 2004) where it has the potential to accumulate.

This study addresses both particle and solution transport of ^{14}C by sampling a range of sites within the area dominated by particle transport and that dominated by solution transport, with particular attention being given to sites north of Sellafield beyond the area dominated by particle transport. In addition, sites south of Sellafield were sampled to investigate any southward transport of ^{14}C. A background value for the west coast UK marine environment was determined, allowing any enrichment in ^{14}C concentration to be identified. The work presented here is a component of a larger study investigating the fate of Sellafield-derived ^{14}C in the marine environment including transport and uptake in intertidal sediments, offshore sediments and marine organisms.

2.2 Methodology

Samples were collected in late 2013/early 2014 from eight intertidal sites on the UK west coast as shown in Figure 2.1. Six of these sites are located north of Sellafield with two (Parton and Allonby) studied previously (Cook *et al.*, 2004b; Muir *et al.*, 2015). Parton and Allonby were chosen to gain an understanding of how the ^{14}C activity in shells/intertidal sediment was responding to changes in discharge over time. The other four northern sites (Kippford, Garlieston, Maidens and Port Appin) are increasingly distant from Sellafield and of these, Maidens and Port Appin are well beyond the area dominated by particle transport of Sellafield-derived radionuclides (Mackenzie *et al.*, 1987) and designated as far-field due to being located north of the North Channel. Two sites south of Sellafield were also sampled (Ravenglass and Barrow).

Several kilograms of surface sediment, including shells, were collected randomly along the high water mark at each of the eight sites. Shell collection was non-species-specific and species were later identified in the laboratory. In addition, mussel shells from recently dead individuals (shells were still hinged) were sourced from Bunbeg on the west coast of Ireland, to provide a measure of contemporary marine inorganic ^{14}C background. This site is geographically close to a background sampling site used previously (Cook *et al.*, 1998), and on the Atlantic coastline, thus virtually free of UK coastal influences.

The sediments were oven dried at 40°C and sieved into four size fractions; >2 mm, 500 µm-2 mm, 63-500 µm and <63 µm. Shell fragments were picked from the >2 mm fraction and homogenised using a mortar and pestle. Common cockle (*Cerastoderma edule*), common periwinkle (*Littorina littorea*) and blue mussel (*Mytilus edulis*) shells were the most ubiquitous whole shells collected across all sites and, where more than two of these shells were available, they were analysed for ^{14}C activity. Cockle shells were available from four, mussel shells from six, and winkle shells from seven sites. The shells were placed in a sonic bath for approximately 10 minutes to remove any adhering sediment and organic matter (i.e. extraneous algae) and then washed thoroughly with distilled water. They were subsequently crushed, homogenised and sub-sampled to provide a single composite sample for each species at each site.

Samples were hydrolysed within a vacuum system using excess 1 M hydrochloric acid (HCl) and the liberated CO_2 was cryogenically purified under vacuum using liquid N_2. Sub-samples (3 mL) of CO_2 were converted to graphite according to the method of Slota *et al.* (1987) and measured on a NEC 250 kV single-stage accelerator mass spectrometry (SSAMS) (Naysmith *et al.*, 2010). A further sub-sample of CO_2 was taken for $\delta^{13}C$ measurement by isotope ratio mass spectrometry using a VG SIRA 11 (Ascough *et al.*, 2012). Results were converted from AMS fraction modern values to specific activity in Becquerel's per kilogram of carbon (Bq kg^{-1} C) using the regime described for enhanced ^{14}C activities in Mook and van der Plicht (1999). Uncertainties are less than 0.5% of the measured activity.

2.3 Results and Discussion

2.3.1 ^{14}C Background Activity

Analysis of a combined sample of 6 hinged mussel shells from the west coast of Ireland produced a ^{14}C activity of 249 ± 1 Bq kg^{-1} C. This value is comparable to the background activity for 1995 published by Cook *et al.* (1998) of 247.6 ± 1.0 Bq kg^{-1} C and indicates a steady-state ^{14}C activity for the marine environment in this area. Mussels predominantly utilise DIC directly from the water column to build their shells, although shell carbon can also be sourced metabolically from their diet (McConnaughey *et al.*, 1997; Gillikin *et al.*, 2006). Due to their selective filter feeding habit, mussels primarily consume phytoplankton, and as phytoplankton also derive carbon from DIC during photosynthesis (Lalli and Parsons 1993), it follows that mussel shell ^{14}C activity will reflect the local ^{14}C concentration in the DIC. The west coast of Ireland is relatively free of UK anthropogenic inputs with water being predominantly Atlantic in origin. This value is therefore used as a background activity and a baseline against which to measure enriched ^{14}C in west coast UK marine samples.

2.3.2 Shell ^{14}C

Results for whole shells are presented in Figures 2.3 (mussel shells), 2.4 (winkle shells) and 2.5 (cockle shells), and in Table 2.1. The highest measured activities across all shell types were at Ravenglass (2350 Bq kg^{-1} C for mussel shells) which, although located south of Sellafield, is the site closest to the reprocessing facility. Despite the net yearly

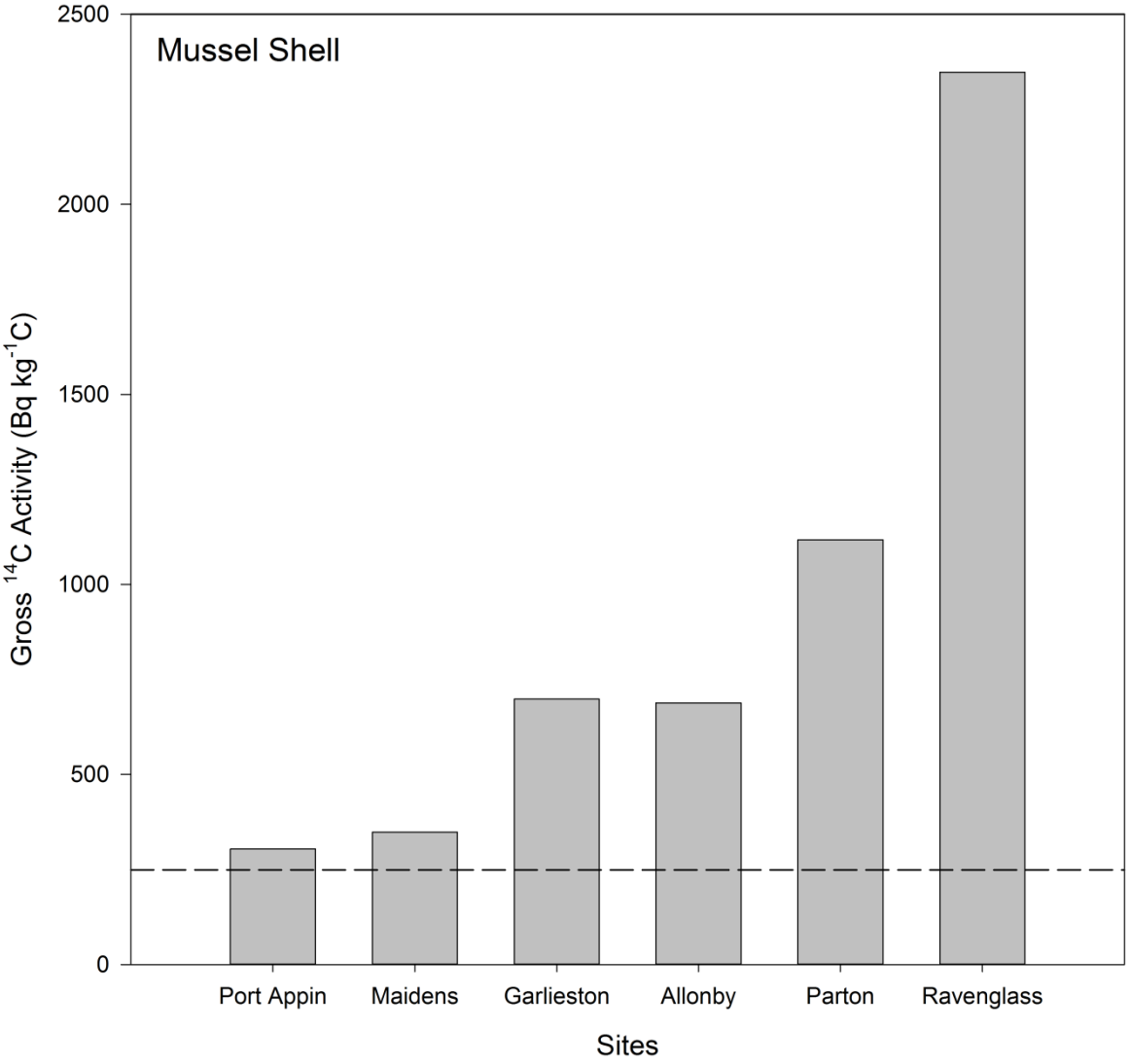

Figure 2.3. Gross ^{14}C specific activities (Bq kg^{-1} C) in mussel shells. The dashed line indicates the measured background activity of 249 Bq kg^{-1} C measured in mussel shells from the West Coast of Ireland. Note that errors are minimal and would not be clearly observable on this scale, they can, however, be seen in Table 2.1.

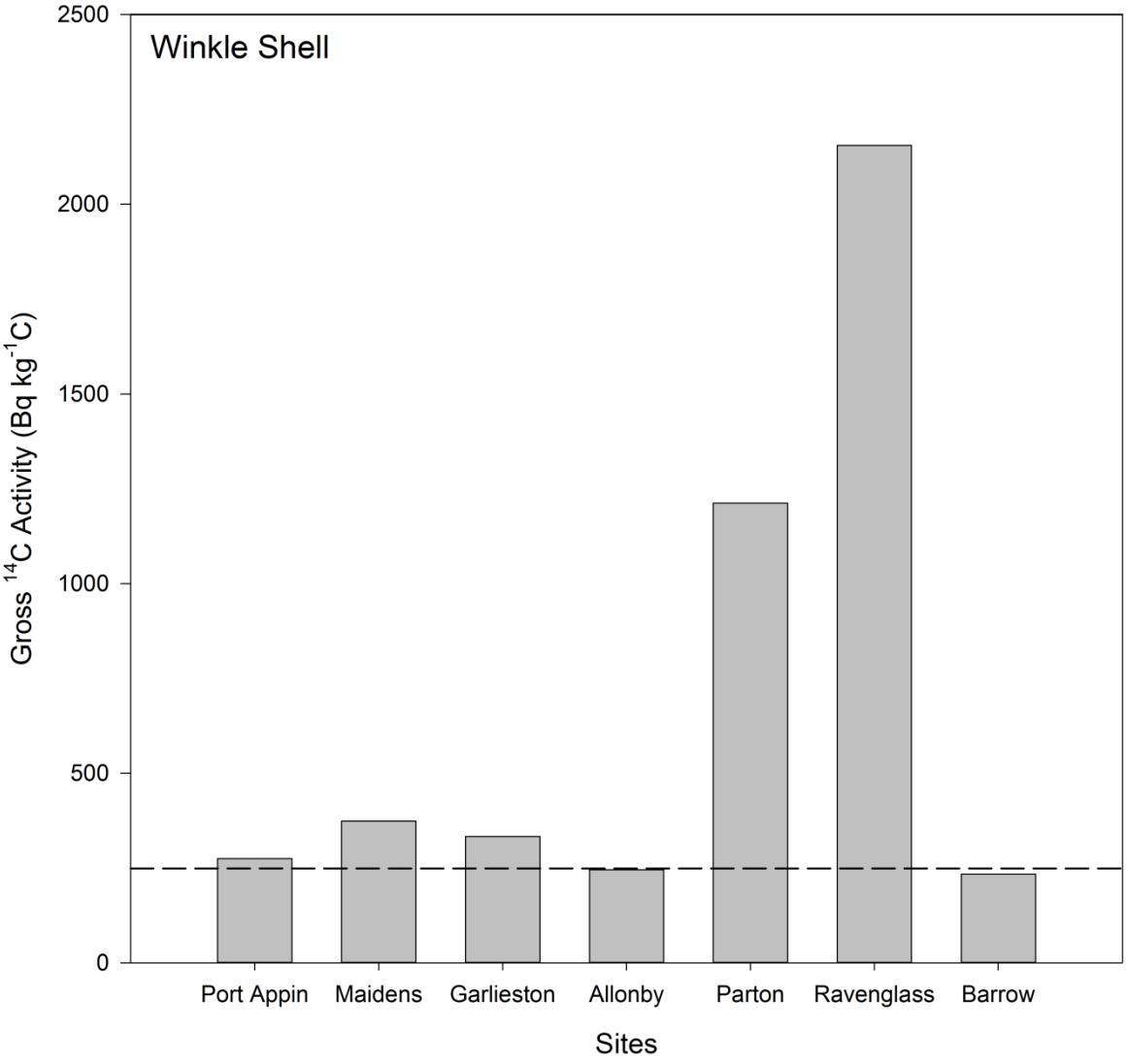

Figure 2.4. Gross ^{14}C specific activities (Bq kg^{-1} C) in winkle shells. The dashed line indicates the measured background activity of 249 Bq kg^{-1} C.

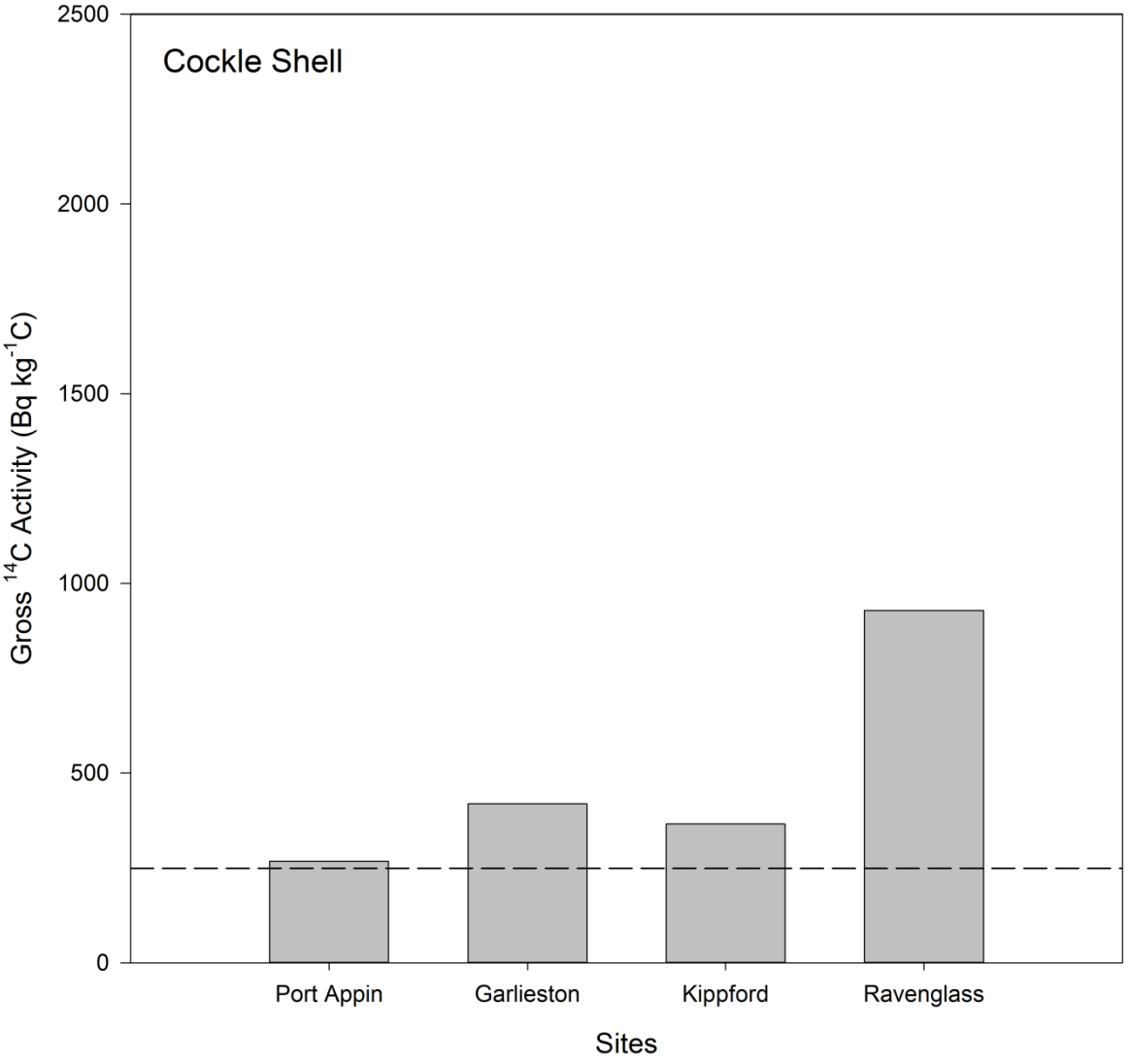

Figure 2.5. Gross ^{14}C specific activities (Bq kg^{-1} C) in cockle shells. The dashed line indicates measured background activity of 249 Bq kg^{-1} C.

northward flow, seasonal southward flow, due to prevailing winds, is known to occur in the Irish Sea (Davies *et al.*, 2002; Dabrowski and Hartnett 2008; Dabrowski *et al.*, 2010), which would disperse discharged effluent south of Sellafield. Only winkle shells were available from the most southern site, Barrow, and were found to have a ^{14}C activity less than background (234 Bq kg^{-1} C), the only site where this was the case. The $\delta^{13}C$ for this sample was -11.4‰ which indicates that these organisms were not living in a truly marine environment and that there is a freshwater carbonate contribution to their shell formation; in comparison, the $\delta^{13}C$ values for all other samples were between -0.5 and +2.8‰, indicative of a marine environment (Keith *et al.*, 1964). The Barrow samples were collected on the Duddon Estuary, fed largely by the River Duddon, which is likely to be the source of this terrestrial/ freshwater $\delta^{13}C$ signal and below-background ^{14}C activity. This reduction in activity below ambient background could be due to a number of factors including dissolution of geological carbonate in the catchment or oxidation of old organic matter in the water column. As Barrow shell fragment activity (discussed in 2.3.3) is above background and produced a marine $\delta^{13}C$ signal (+0.1) it is probable that the whole winkle shells are not representative of the environment they were found in and have been washed downstream from a site closer to the river mouth. At other sites, whole shell activities generally reduce moving north from Sellafield but remain above background. All shell types found at the two far-field sites (Maidens and Port Appin) were enriched, indicating significant ^{14}C enrichment of the DIC component of Scottish coastal water. A preliminary result of direct analysis of the DIC component of water in the Firth of Lorn (West Scotland) in spring 2014 (298 Bq kg^{-1} C) confirms this enrichment.

Mussel shells typically had the highest activities at each site (average for all sites = 917 Bq kg^{-1} C) followed by winkle (690 Bq kg^{-1} C) and then cockle shells (495 Bq kg^{-1} C). The disparities between species may be explained to some extent by their respective ecologies. Mussels are filter feeders predominantly feeding on phytoplankton which derive all their carbon from DIC. Winkles graze on algae and some intertidal algae such as sea lettuce (which is a known food source for winkles), can utilise atmospheric carbon when exposed to the atmosphere (Murthy *et al.*, 1987). The influence of Sellafield on the atmospheric ^{14}C activity only extends to around 10 km from the plant, thereafter, the activity is greatly diluted and the general atmospheric activity is relatively constant (McCartney *et al.*, 1988). The ^{14}C activity of terrestrial vegetation is a good proxy for

Table 2.1. Gross ^{14}C specific activities in intertidal shells and sediments (Bq kg^{-1} C). The $\delta^{13}C$ values are relative to VPDB (Craig 1957).

	Sampling Site							
Sample Type	**Port Appin**	**Maidens**	**Garlieston**	**Kippford**	**Allonby**	**Parton**	**Ravenglass**	**Barrow**
	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)	^{14}C (Bq kg^{-1} C) ($\delta^{13}C$ ‰)
Whole Shells								
Mussel Shells	304 ± 2 (0.5)	348 ± 2 (0.7)	698 ± 3 (2.2)	na	688 ± 3 (-0.4)	1120 ± 5 (-0.2)	2350 ± 11 (-0.5)	na
Cockle Shells	267 ± 1 (0.3)	na	418 ± 2 (2.8)	365 ± 2 (0.2)	na	na	929 ± 6 (-0.1)	na
Winkle Shells	275 ± 1 (0.7)	374 ± 2 (0.3)	333 ± 2 (0.4)	na	245 ± 2 (1.5)	1210 ± 5 (0.6)	2160 ± 9 (0.5)	234± 1 (-11.4)
Sediment								
Shell fragments (>2 mm)	273 ± 1 (1.0)	334 ± 2 (0.1)	302 ± 2 (0.7)	322 ± 2 (0.3)	527 ± 2 (-0.1)	444 ± 2 (2.0)	627 ± 3 (-2.5)	290 ± 1.0 (0.1)
Sediment 500 µm-2 mm	276 ± 1 (0.9)	241 ± 1 (-0.7)	224 ± 1 (0.2)	427 ± 2 (0.1)	223 ± 1 (0.6)	152 ± 1 (1.8)	161 ± 1 (0.6)	22.0 ± 0.1 (0.2)
Sediment 63-500 µm	17.7 ± 0.1 (-1.7)	86.8 ± 0.3 (0.9)	92.9 ± 0.4 (-1.6)	283 ± 1 (-0.2)	139 ± 1 (1.6)	214 ± 1 (0.0)	194 ± 1 (-1.4)	14.0 ± 0.1 (0.1)
Sediment <63 µm	44.9 ± 0.2 (1.0)	87.8 ± 0.3 (-2.9)	63.7 ± 0.2 (0.2)	115 ± 1 (-0.4)	308 ± 2 (-0.3)	443 ± 2 (0.1)	174 ± 1 (-2.8)	31.2 ± 0.1 (-1.1)

na – no species available

atmospheric activity and the ^{14}C activity of a Scottish barley mash (a bi-product of the whisky industry) from 2013, was 229 Bq kg^{-1} C, significantly lower than the DIC ^{14}C activity measured at sites remote from Sellafield, such as the Firth of Lorn (298 Bq kg^{-1} C). The lower atmospheric ^{14}C activity would result in a reduced algal activity relative to the DIC. As some of the carbon used in shell building by marine molluscs is metabolically derived, this will manifest itself in a reduced winkle shell ^{14}C activity relative to mussel shells. Cockles have the lowest activity although the reason for this is less obvious. Like mussels, cockles are filter feeders and will be sourcing similar food-stuffs at the same sites. However, mussels and winkles inhabit surface environments whereas cockles bury themselves in the sediment. It would seem unlikely that cockles are sourcing less enriched DIC from sediment pore water in their immediate vicinity as they are only shallow burrowers (typically down to 5-10 cm maximum) and it is well established that the sediments are well mixed to significant depths primarily due to bioturbation (Kirby *et al.*, 1983), hence, the pore water here is likely to be well mixed with water overlying the sediment. However, the ^{14}C activity of the organic component of surface sediments can be significantly depleted. For example, Wolstenhome *et al*. (1998) demonstrated depletion in surface sediments of the NE Irish Sea while the particulate organic carbon (POC) and DIC fractions of the water column were enriched above the ambient background value. Therefore, if organic matter in the surface sediment contributes some carbon to shell formation, this could account for the lower activities.

2.3.3 Sediment ^{14}C

Results for sediment fractions are presented in Figure 2.6 and Table 2.1. Shell fragments were enriched above background at all sites, including Barrow. Large shell fragments are unlikely to have been transported from sites closer to Sellafield and suggest that whole shells in this area, and therefore DIC, were above background. Circulation models have suggested that seasonal southward flow of water will disperse dissolved radionuclides from Sellafield as far as Liverpool Bay (Dabrowski and Hartnett 2008). The highest measured activity was again south of Sellafield at Ravenglass (627 Bq kg^{-1} C in shell fragments). Overall, ^{14}C activity generally decreases with distance from Sellafield. At far-field sites, enhanced activities were found in shell fragments at Maidens (334 Bq kg^{-1} C) and Port Appin (273 Bq kg^{-1} C) with the 500 µm-2 mm fraction also enriched at the latter site (276 Bq kg^{-1} C). As the higher-activity, whole shells are

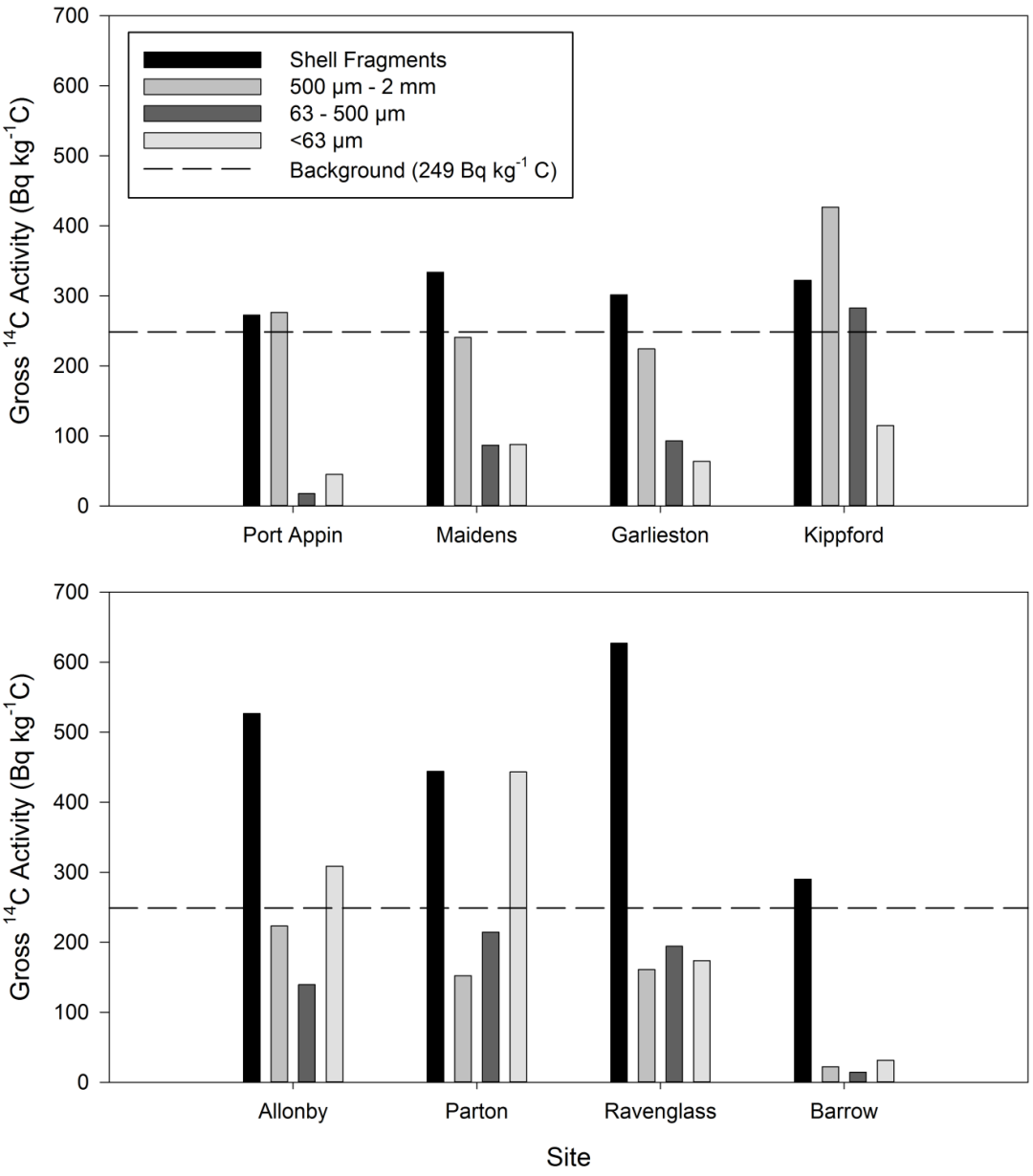

Figure 2.6. Gross ^{14}C specific activities (Bq kg^{-1} C) in different size fractions of the carbonate component of Scottish (top) and English (bottom) west coast intertidal sediments.

gradually broken down by in-situ erosion, the finer material that is produced will be incorporated into the sediment, gradually increasing its activity (Cook *et al.,* 2004b). This is on the assumption that whole shells break down to coarse fragments and subsequently to finer and finer size fractions. If in-situ erosion of shells is the predominant source of ^{14}C to sediment, it follows that currently, there should be a general reduction in activity with decreasing particle size as there will be a larger proportion of older (and therefore less enriched) material within the finer sediment fractions (Cook *et al.,* 2004b). However, this is not the case for several sites and is particularly evident at Allonby and Parton. At these sites, shell fragments and the finest sediment (<63 μm) were found to be enriched above background but both intermediate sediment sizes (500 μm-2 mm and 63-500 μm) had activities that were lower than the ambient background. Similar results were found in 2011 by Muir *et al.* (2015) at Parton and another site not investigated in the present study (Flimby). Two possible mechanisms for this enrichment of finer material were proposed: 1. greater northwards movement in the water column of the finest fraction compared to coarse material, or 2. rapid breakdown of the shell material at these sites. The second mechanism could also involve the gradual weathering of a shell surface, where fine material is eroded off rather than shell breakdown to intermediate particle sizes. The inside surface of some mollusc shells including mussels and winkles, is made from strong aragonite layers called nacre. This could take longer to erode than other calcified layers which break down relatively quickly and contribute to sediment enrichment.

2.3.4 Intertidal ^{14}C Activity 2001 – 2014

As noted in section 2.2, two sites in the current study have been investigated previously; Parton and Allonby. These sites were first visited in 2001 (Cook *et al.,* 2004b) and again in 2011 (Muir *et al.,* 2015). The measured ^{14}C activities at these sites in the current and previous studies are presented in Figure 2.7. At Parton, both mussel shell and coarse sediment (>500 μm) activities increased between 2001 and 2011, before decreasing in 2014. The intermediate sediment (63-500 μm) activity increased between each study whereas there is little change in fine sediment (<63 μm) activity. At Allonby, mussel shell activity again increases between 2001 and 2011 and decreases by 2014. All sediment fractions increased in activity towards 2014, most significantly in the finest fraction (<63 μm) between 2011 and 2014.

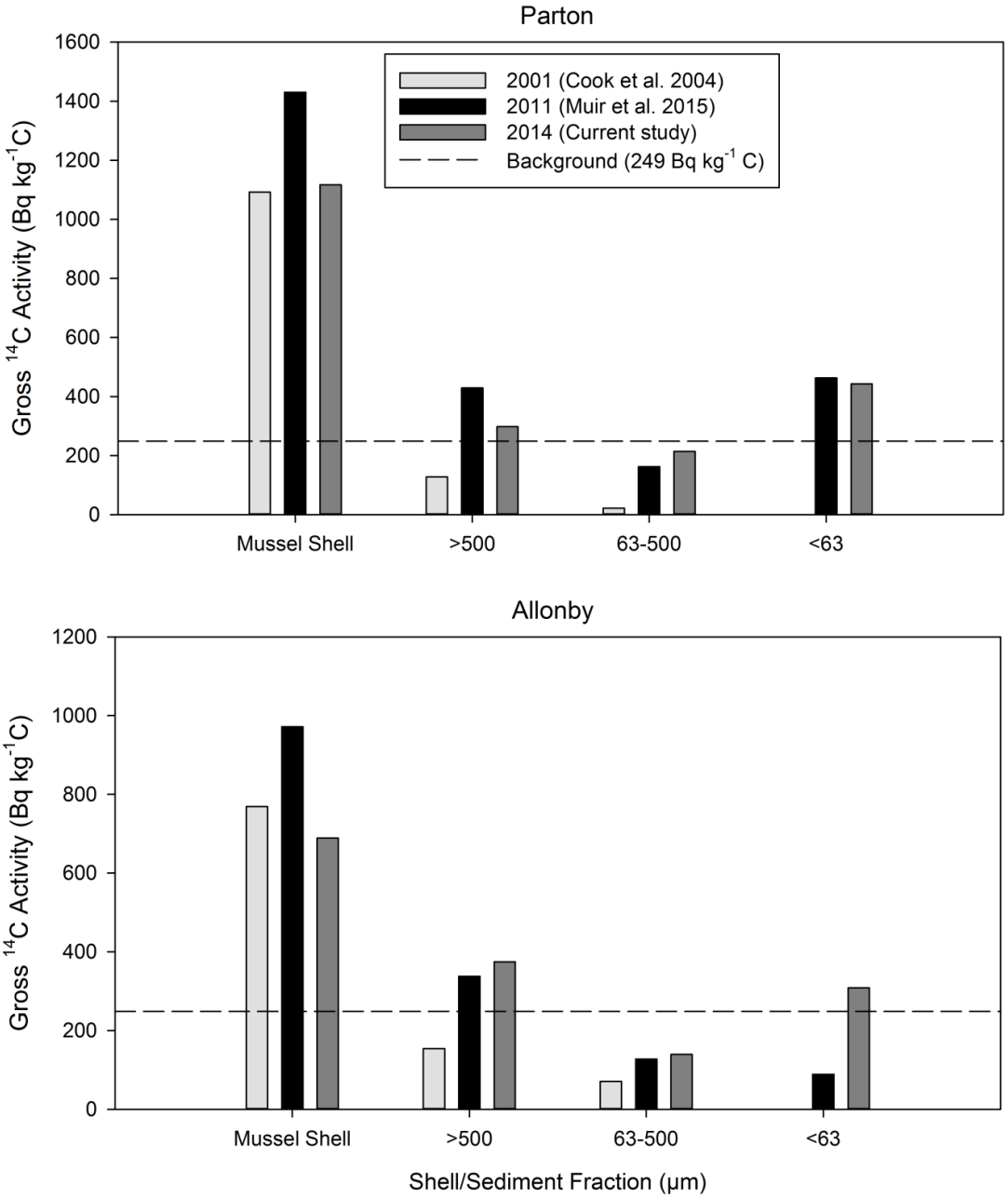

Figure 2.7. Gross ^{14}C specific activities (Bq kg^{-1} C) in mussel shells and intertidal sediment fractions at Parton (top) and Allonby (bottom). The >500 µm fraction for the current study is an average of shell fragments (>2 mm) and the 500 µm – 2 mm sediment fraction. No data is available for the <63µm sediment fraction from 2001.

The shell lengths of mussel shells used in this study were typically 5-6 cm, meaning the mussels would have been about 5 years in age (Bayne and Worrall 1980). If, for the three studies, the mean aquatic ^{14}C discharged activity for the 5 years prior to sampling is compared to the whole mussel shell activities, it can be observed that mussel shell activity responds in accordance with discharge activity (Table 2.2). The activity of whole mussel shells at Parton increased from 1090 Bq kg^{-1} C in 2001 to 1430 Bq kg^{-1} C in 2011 in response to an increase in the 5 year average discharge from 5.93 TBq y^{-1} to 7.06 TBq y^{-1}. This was followed by a reduction in mussel shell activity in 2014 to 1120 Bq kg^{-1} C, corresponding to a reduction in average discharge over the previous 5 years to 5.71 TBq. A similar pattern in ^{14}C activities is observed at Allonby.

Table 2.2. Mussel shell activities at Parton and Allonby over three studies and the corresponding average marine ^{14}C discharge (TBq) from Sellafield in the 5 years prior to shell collection in each study.

Year of Shell Collection (study)	**Mussel Shell Activity (Bq kg^{-1} C)**		**5 Year Average Sellafield Marine Discharge Previous to Collection Date (TBq)**
	Parton	**Allonby**	
2001 (Cook *et al.*, 2004)	1090	769	5.93
2011 (Muir *et al.*, 2015)	1430	972	7.06
2014 (present study)	1120	688	5.71

The increasing activity in sediment fractions at Allonby (which is also apparent in the intermediate fraction at Parton) supports the hypothesis that as whole shells erode they will contribute enhanced ^{14}C activities to the sediment. However, a considerable change is found in the finest sediment at Allonby, from ^{14}C-depleted in 2011 (89 Bq kg^{-1} C) to significantly enriched in this study (308 Bq kg^{-1} C). It is unlikely that the difference between these two studies could be solely explained by erosional processes within the time interval of about 3 years. Although, it is possible that this difference could be the result of sampling location on site, a more likely explanation may be offered by particle transport processes. Fine, highly enriched particulate material from sites closer to Sellafield may be re-suspended (possibly during storm events), transported northwards with prevailing currents and re-deposited at Allonby. This would be consistent with northward currents and known northward movement of sediment within the Irish Sea (Mackenzie *et al.*, 1987, 1994, 1998, 1999; McDonald *et al.*, 1990; Cook *et al.*, 1997).

The selective particle transport of fine material over coarser material from more enriched areas may help explain the relatively high activities found in finer material at other sites including Parton. The pre-existing ^{14}C enriched activity at Parton may be due to previous sedimentary deposition of enriched material. Subsequently, there was no observed ^{14}C increase in the finest sediment fraction at Parton between 2011 and 2014 as the activity of any newly deposited material was similar.

2.4 Conclusions

The results of this study suggest that the ^{14}C activity in whole mussel shells at two previously-investigated sites on the NE Irish Sea coast, north of Sellafield, are varying in response to the average ^{14}C discharge over the preceding 5 years. In contrast, there is a general increase in the ^{14}C activity of the finer fractions of the inorganic intertidal material, confirming the previous hypothesis of an increased activity in fine material as whole shells/larger fragments formed during the nuclear era are broken down over time. Consequently, the ^{14}C activity of the inorganic carbon component of intertidal and sub-tidal NE Irish Sea sediments will gradually increase. The ^{14}C activity of shell fragments at all Scottish sites were also enriched relative to ambient background (with the 500 μm – 2 mm fraction close to ambient background), suggesting that a similar trend will be observed in time at these more remote sites. On average, the ^{14}C activity in whole shells follows the trend of mussels > winkles > cockles which reflects their feeding habits and the ecological niche they occupy.

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Chapter 3
Ecosystem uptake and transfer of Sellafield-derived Radiocarbon (^{14}C)
Part 1. The Irish Sea

Abstract

Ecosystem uptake and transfer processes of Sellafield-derived radiocarbon (^{14}C) within the Irish Sea were examined. Highly variable activities in sediment, seawater and biota indicate complex ^{14}C dispersal and uptake dynamics. All east basin biota exhibited ^{14}C enrichments above ambient background while most west basin biota had ^{14}C activities close to background, although four organisms including two slow-moving species were significantly enriched. The western Irish Sea gyre is a suggested pathway for transfer of ^{14}C to the west basin and retention therein. Despite ongoing Sellafield ^{14}C discharges, organic sediments near Sellafield were significantly less enriched than associated benthic organisms. Rapid scavenging of labile, ^{14}C-enriched organic material by organisms and mixing to depth of ^{14}C-enriched detritus arriving at the sediment/water interface are proposed mechanisms to explain this. All commercially important fish, crustaceans and molluscs showed ^{14}C enrichments above background; however, the radiation dose from their consumption is extremely low and radiologically insignificant.

This chapter has been published as:

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3.1. Introduction

3.1.1 Sellafield

The Sellafield nuclear complex, situated on the Cumbrian coast of the north-east Irish Sea (Figure 3.1), undertakes reactor decommissioning, fuel reprocessing and storage of nuclear materials, including radioactive wastes. During reprocessing operations, radioactive wastes are discharged to the sea and atmosphere, or disposed of as solid waste (Nuclear Decommissioning Authority, 2014). Aquatic radioactive discharges are made via pipelines extending 2.1 km into the north-east Irish Sea. Sellafield (then Windscale) commenced discharges of low-level radioactive waste, including ^{14}C, to the north-east Irish Sea in 1952, with peak discharges for most radionuclides occurring in the early- to mid-1970s (Gray *et al*., 1995). Extensive research into the fate of discharges to the Irish Sea has demonstrated that an area of fine offshore sediment (known as the Sellafield mudpatch), close to the discharge point, has acted as an important sink for radioactive contaminants (Pentreath *et al*., 1984; Kershaw *et al*., 1992; Cook *et al*., 1997; Hunt *et al*., 1998; MacKenzie *et al*., 1987, 1999, 2000). Since the 1970s, liquid radioactive discharges have fallen significantly with the introduction of several waste treatment plants that are efficient at removing cationic fission products e.g. $^{137}Cs^{+}$ and actinides from waste effluent, but ineffective at removing most anionic species such as $^{14}CO_3^{2-}$ (Gulliver *et al*., 2001). One notable exception is the pertechnetate ($^{99}TcO_4^{-}$) abatement technology, introduced in 2003, which is efficient at removing anionic ^{99}Tc from the effluent stream (RIFE-9, 2004). Waste radiocarbon (^{14}C) is produced during the nuclear fuel cycle from a range of neutron capture reactions, but predominantly from nitrogen impurities in the fuel and cladding involving the ^{14}N (n, p) ^{14}C reaction (Otlet *et al*., 1990, 1992). ^{14}C is either stored in waste repositories or discharged, under authorisation, to the environment as low-level waste (LLW).

3.1.2 Sellafield-derived ^{14}C

Due to the ineffectiveness of the waste treatment plants in removing most anionic species, the pattern of temporal variations in the quantities of ^{14}C discharged to the Irish Sea has differed from most other radionuclides. Up to 1984, aquatic discharges of ^{14}C from Sellafield (Figure 3.2) were estimated and were subsequently measured between

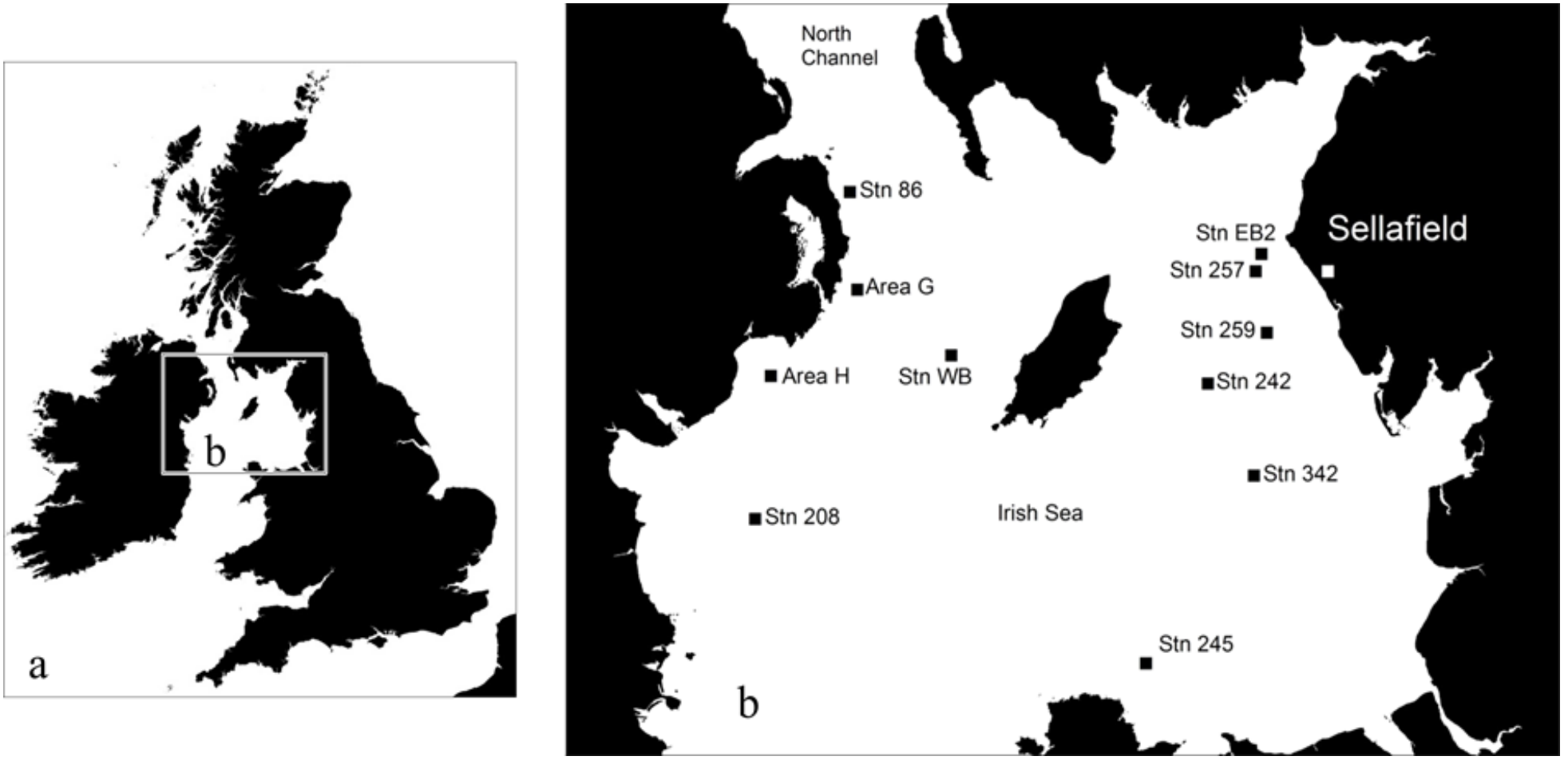

Figure 3.1. Map of the British Isles (a) and inset of the Irish Sea (b) indicating sampling sites.

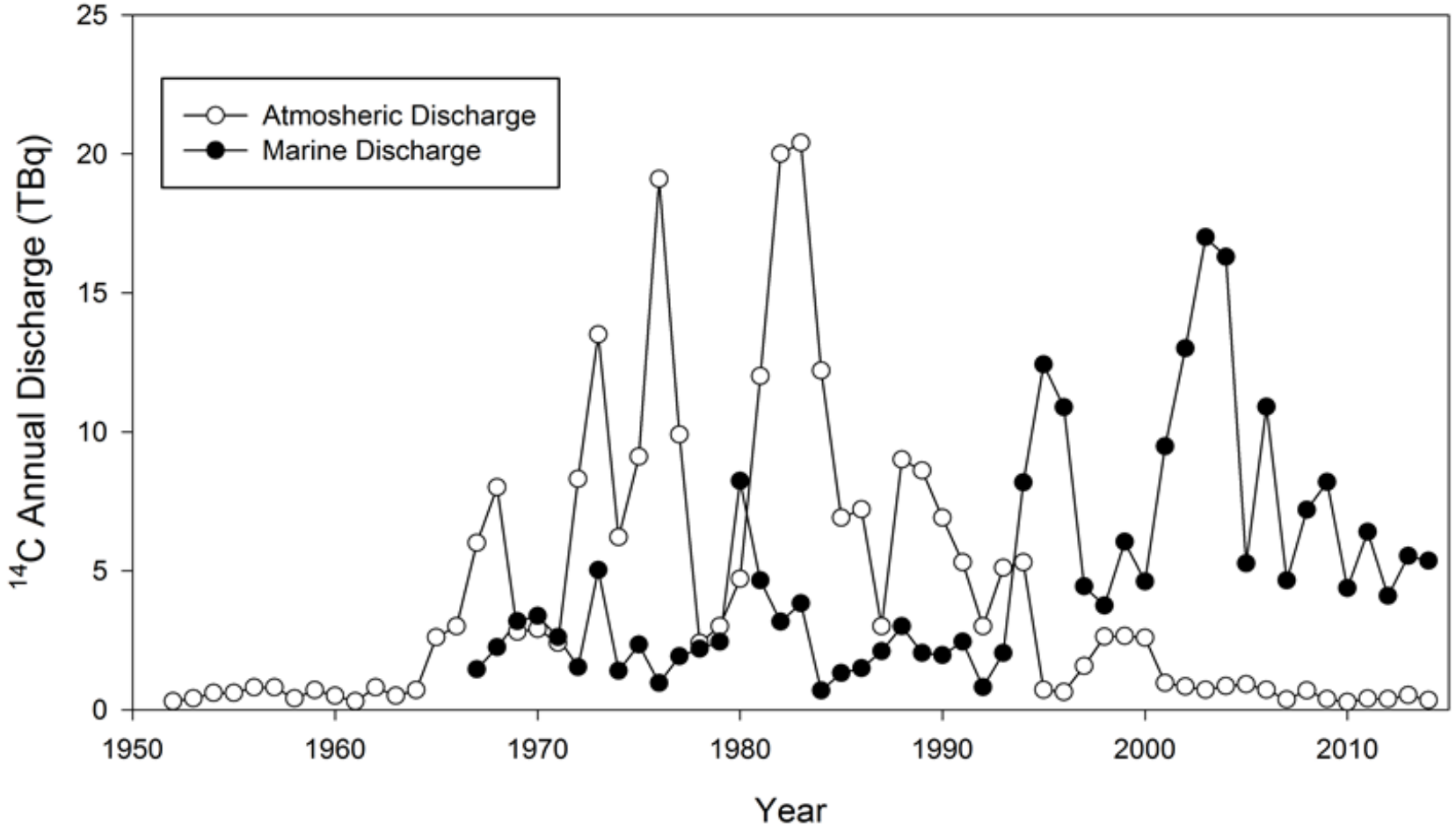

Figure 3.2. Sellafield atmospheric and marine ^{14}C discharges (TBq) between 1968 and 2014. Data prior to 1985 are estimated (Cook *et al*., 2004). Subsequent measured data were taken from BNFL (1985-1989); MAFF (1992-1995) and RIFE (1996-2015) reports.

1984 and 1993 at < 2 Tera Becquerels (TBq) per year, on average, until 1994 when ^{14}C discharges increased by an order of magnitude (BNFL 1985-1989; MAFF 1992-1995). This increase was partly due to a change in discharge policy, diverting atmospheric ^{14}C discharges to the aqueous route, and to a lesser extent to an increase in reprocessing activity as the thermal oxide reprocessing plant (THORP) began operations (BNFL, 2002). Between 1994 and 2014, Sellafield discharged a total of 166.9 TBq of ^{14}C to the Irish Sea, with an average annual discharge of 7.9 TBq (MAFF, 1994, 1995; RIFE (1-20)1996-2015). Sellafield ^{14}C marine discharges contribute 4.8% (2.8 μSv) to the current total dose (58 μSv) received by the critical group of consumers of marine fish and shellfish from the Cumbrian coast, which is small when compared with the average annual dose (2230 μSv) received by an individual in the UK from natural sources of radioactivity (Nuclear Decommissioning Authority, 2015). However, due to the long half-life of ^{14}C (5730 y) and ready entry into the global carbon cycle, aquatic ^{14}C discharges are the dominant contributor to collective doses (man Sievert (man Sv)) for UK (0.94 man Sv), European (3.1 man Sv) and World (32 man Sv) populations from total contributions of 1.2, 3.7 and 33 man Sv, respectively, resulting from the effects of all discharges from Sellafield in 2014 (Nuclear Decommissioning Authority, 2015). According to UNSCEAR (2008), liquid ^{14}C discharges from global fuel reprocessing, between 1998 and 2002, contributed 94% of the total collective dose from all radionuclides. Furthermore, the largest total dose estimates from the nuclear industry remain associated with releases of ^{14}C.

Sellafield ^{14}C discharges are additional to an existing 'background' pool of ^{14}C derived from natural production and atmospheric testing of atomic weapons, primarily during the 1950s and 1960s. This ^{14}C 'background' level for north-east Atlantic biota and dissolved inorganic carbon (DIC) was measured in 1995 at 248 ± 1 Bq kg^{-1} (Cook *et al*., 1998). Tierney *et al*. (2016) redefined this value in 2014, based on analyses of blue mussel (*Mytilus edulis*) shells collected on the west coast of Ireland, and obtained an almost identical background value of 249 ± 1 Bq kg^{-1}, which is the value used in this study.

^{14}C is discharged to the Irish Sea primarily as dissolved inorganic carbon (DIC) (Begg *et al*., 1991, 1992; Begg, 1992; Cook *et al*., 1995). It is rapidly incorporated into the general DIC component of seawater and is largely dispersed in solution from the Irish Sea through the North Channel by prevailing residual northerly currents (Gulliver *et al*., 2001). However, a small but poorly characterised component of the ^{14}C is retained in

Irish Sea biota and sediment (MacKenzie *et al*., 2004). Unlike most other radionuclides, ^{14}C dispersion cannot be explained by a sorption coefficient (K_d). Soluble ^{14}C in DIC is readily utilised through fixation of $H^{14}CO_3^-$ and $^{14}CO_3^{2-}$ by primary producing organisms (phytoplankton and macroalgae) during photosynthesis (Lalli and Parsons, 1993) and is thus a bioavailable 'contaminant' which is transferred through the entire marine food chain and will be manifested as particulate organic carbon (POC). Most POC is produced autochthonously from *in situ* decay of phytoplankton produced in the euphotic zone, and is otherwise comprised of detritus, including faecal pellets, dead organisms and organic aggregates of various types. Thus, ^{14}C is subsequently transferred from the DIC to the POC reservoir and to the dissolved organic carbon (DOC) reservoir from *in situ* processes including exudation by phytoplankton, secretion from zooplankton, after-death decay processes and from external terrestrially derived sources (Chester, 1990). Additionally, marine calcifying organisms e.g. molluscs, foraminiferans and coccolithophorids efficiently utilise DIC directly from the water column during shell (or plate) formation (Chester, 1990, McConnaughey *et al*., 1997) providing an uptake pathway for inorganic ^{14}C into the particulate inorganic carbon (PIC) reservoir (Cook *et al*., 2004; Muir *et al*., 2015; Tierney *et al*., 2016). Inorganic carbonate material is broken down after death of the organism, and is removed by settling from surface waters. Eventually, organic and inorganic particulate material will be deposited to some degree into offshore sediment.

Concern over the radiological importance of ^{14}C has prompted several investigations into the behaviour and distribution of ^{14}C in the Irish Sea environment (Begg *et al*., 1991, 1992; Begg, 1992; Cook *et al*., 1995, 1998, 2004; Wolstenholme *et al*., 1998; Wolstenholme, 1999; Gulliver *et al*., 2001; Gulliver, 2002). This research revealed ^{14}C enrichment in the biogeochemical (carbon) fractions of seawater, sediments and biota. ^{14}C activities in the biogeochemical fractions (post-1994 discharge policy change) were typically greater than pre-1994 levels (Begg *et al*., 1992; Cook *et al*., 1995, 2004). ^{14}C exhibited conservative behaviour in the DIC component of seawater (Begg, 1992), with some evidence of transfer into the other biogeochemical fractions, although no systematic trend was observed between the DIC activity and that of the other fractions. At this time, incorporation of ^{14}C was observed in north-east Irish Sea demersal fish and mussels, demonstrating systematic ^{14}C enrichment relative to ^{14}C activities in DIC and plankton (Begg *et al*., 1992; Cook *et al*., 1995). This anomaly was attributed to mussels and fish integrating ^{14}C activities, associated with plankton and other organic detritus,

over several bloom periods, possibly coinciding with a period of high ^{14}C discharge (Cook *et al*., 1995). Significant ^{14}C enrichments observed in the seawater DIC pool and biota were largely confined to the NE Irish Sea (Cook *et al*., 1998). Beyond the North Channel, ^{14}C activities decreased with increasing distance from Sellafield. Differences in ^{14}C activities between species were attributed to the variability in the kinetic response of biota to changing ^{14}C discharges, and to the differences in the pools from which biota derived their carbon. These mechanisms have been confirmed by examination of species-specific feeding habits in relation to ^{14}C activity trends and enhancements in intertidal biota (Cook *et al*., 2004). Similar trends were evident in shells of Irish Sea intertidal molluscs (Muir *et al*., 2015) and in molluscs at sites remote from Sellafield dominated by solution transport of ^{14}C (Tierney *et al*., 2016). These studies demonstrate a net overall increase in ^{14}C in the inorganic component of north-east Irish Sea intertidal sediments. Nevertheless, ^{14}C activities in offshore sedimentary carbonates remain low (Gulliver *et al*., 2001, Gulliver, 2002; Wolstenholme *et al*., 1998, 1999), in comparison to the organic component of sediment, which has specific ^{14}C activities approximately twice that of the ambient background level (Gulliver, 2002). This provides unambiguous evidence of systematic Sellafield ^{14}C contamination in the Irish Sea (MacKenzie *et al*., 2004).

Routine monitoring of specific activities of marine organisms close to the discharge pipeline are reported annually by Sellafield (BNFL, 1971- 2004; BNGSL 2005, 2006; Nuclear Decommissioning Authority (Sellafield Ltd.), 2007-2015), the Ministry of Agriculture Fisheries and Food (MAFF 1967-1995) and then a later partnership of the Food Standards Agency, Food Standards Scotland, the Environment Agency, the Scottish Environment Protection Agency, Natural Resource Wales and the Northern Ireland Environment Agency (RIFE, 1996-2015). Since 1986, and up to the most recent publication for 2015, continued local enhancements in ^{14}C activity have been observed in north-east Irish Sea organisms due to discharges from Sellafield (MAFF 1987-1995; RIFE, 1996-2015).

As a consequence of the past and ongoing Sellafield marine ^{14}C discharges, UK coastal waters present a unique opportunity to investigate the concentration, distribution and environmental behaviour of ^{14}C. Accurate knowledge of these factors is critical when evaluating historical, contemporary and emergency releases of ^{14}C to the marine environment in terms of human radiation exposure, via marine food web transfer, and is

of fundamental importance for planning, management and regulation of nuclear facilities.

In consideration of Sellafield's ongoing aqueous ^{14}C discharges, the work presented here, over two-parts, examines the environmental behaviour and processes of ^{14}C in two distinct marine ecosystems defined according to geographical location (relative to Sellafield), oceanographic conditions and processes, and the diversity of species found within each setting. Part 1 (this study) investigates processes in the Irish Sea; whilst sites remote from Sellafield, in the west coast of Scotland, are discussed in Part 2 (Tierney *et al*., 2017).

Specifically, the objectives of this study (Part 1. The Irish Sea) were: i) investigate the marine dispersion of ^{14}C and aqueous phase and solid/ particulate phase partitioning; ii) examine the transfer and extent of ^{14}C incorporation into biotic (benthic, pelagic and planktonic) and abiotic ecosystem components (sediment/ seawater ^{14}C biogeochemical fractions); iii) explore evidence of trophic transfer of ^{14}C by examining complex marine food webs and species ecology; and iv) provide an accurate dose rate assessment to critical groups from consumption of ^{14}C in commercially important organisms. Ultimately, the work presented in this study will contribute to an ongoing novel modelling approach to map the ecological fate of Sellafield-derived ^{14}C.

3.1.3 Study area

The Irish Sea (Figure 3.1) is a semi-enclosed continental shelf sea measuring *ca.* 300 km (160 n.m.) in length and 75 – 195 km (40 – 105 n.m.) in width, decreasing to 30 km (16 n.m.) at the north end in the North Channel (Bowden, 1980). The total volume is estimated at 2430 km^3, with approximately 80% of this volume lying to the west of the Isle of Man (Dickson and Boelens, 1988). An open-ended north /south channel of between 80 – 275 m in depth is located from 5^oW with shallower (30 – 50 m) embayments in the eastern Irish Sea. The north-east Irish Sea basin, the main region of interest in this study, is *ca.* 30 m in depth. The western channel (or basin) is open ended and connected via St. Georges Channel to the Celtic Sea and the Atlantic Ocean at its broad southern boundary. In the north, the Irish Sea is connected via the North Channel to the Clyde Sea and Malin Shelf, which in turn communicates with the Atlantic Ocean through a narrow section of channel of 20 km (11 n.m.) width (Bowden, 1980). Atlantic

water enters the Irish Sea from both channels, forming a complex system where these currents interact, and where wind and density-driven circulation also play important roles (Dabrowski *et al*., 2012). The long-term circulation is predominantly northwards, with inflow through St. George's Channel and outflow via the North Channel (Ramster and Hill, 1969; Howarth, 1982; Gulliver *et al*., 2001). This is consistent with the dispersal patterns of conservative radionuclides (e.g. ^{137}Cs and ^{3}H) which are dominantly distributed according to the movement of major tides and residual currents (Baxter *et al*., 1979; McKay and Baxter, 1985; McDonald *et al*., 1990; Cook *et al*., 1997). However, the net northerly flow is seasonally highly variable and under certain wind-driven conditions is reversed southwards (Dabrowski *et al*., 2010). ^{14}C enhancements observed in intertidal biota both to the north and south of the Sellafield discharge point support this assertion (Begg *et al*., 1991, 1992; Cook *et al*., 2004; Muir *et al*., 2015; Tierney *et al*., 2016), although it is unclear whether radionuclide transport is forced by long-term net circulation or short-term wind and tide-induced water movement. Dickson and Boelens (1988) describe a residual southerly drift along the Cumbrian coast which eventually turns west and then north. However, the time-averaged circulation in the Irish Sea is relatively weak and shows no specific directionality over large areas (Nichols *et al*., 1993). Salinity distributions suggest that exchange between the eastern and western Irish Sea is limited although radionuclide distributions indicate some east to west transport (Leonard *et al*., 1997), probably to the north of the Isle of Man (Gowen *et al*., 2005). Well-defined, thermal stratification occurs in summer in regions of weak currents, notably to the west of the Isle of Man where cold dense water left over from the previous winter is trapped in topographic depressions (Dabrowski *et al*., 2010). As a result of thermal stratification, a density-driven cyclonic gyre forms in deep water (>100 m) in the west basin (Hill *et al*., 1994) and may have significant implications for the retention time of planktonic larvae (Hill *et al*., 1996) and juvenile pelagic fish (Dickey-Collas *et al*., 1997), and the transport and fate of radionuclides and other contaminants (Horsburgh *et al*., 2000; Dabrowski and Hartnett, 2008). Thermal stratification also occurs in the shallow north-eastern basin but is transient and readily overturned by tidal mixing and storms.

Irish Sea surface sediments are dominated by glacial and postglacial material (Pantin, 1977). Muddy sediments occur in areas of low tidal energy and are found off the Cumbrian coast and extensively in the western Irish Sea. Coarser-grained sediments are found to the north and south of the Isle of Man (Kershaw *et al*., 1999). Muddy north-east

Irish Sea subtidal sediments are subject to extensive mixing (MacKenzie *et al*., 1997, 1998, 2004; Kershaw *et al*., 1983, 1984) with very low (max. 0.08 cm yr^{-1}) sedimentation rates in this region (Kershaw *et al*., 1986, 1988). Benthic organisms are responsible for the intensive mixing (bioturbation) observed in the upper 5-10 cm of these sediments (Kershaw *et al*., 1999) and for the subsequent burial of particle-reactive radionuclides that are strongly associated with fine-grained sediment (MacKenzie *et al*., 1999). Bioturbation by the echiuran spoon-worm (*Maxmuelleria lankesteri*), for example, has resulted in the redistribution of Sellafield-derived radionuclides to a depth of 140 cm (Kershaw *et al*., 1983, 1984). Net deposition of fine sediment has been observed in the western basin (Condren *et al*., 1995) and bioturbation, by *Nephrops norvegicus* (Norway lobster; henceforth referred to as *Nephrops*) in particular and by fishing, are influential physical processes in this area (Kershaw *et al*., 1999). The diverse habitats of the Irish Sea support many important fishery species including shellfish e.g. *Nephrops*, king scallop (*Pecten maximus*) and queen scallop (*Chlamys operculari*), flatfish e.g. sole (*Solea solea*), plaice (*Pleuronectes platessa*), brill (*Scophthalmus rhombus*), turbot (*Scophthalmus maximus*) and gadoids e.g. cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus*) and whiting (*Merlangius merlangus*) (CEFAS, 2005).

3.2 Methodology

3.2.1 Sampling and analysis

Seawater biogeochemical carbon fractions (DIC, DOC, PIC, POC), sediment, benthic organisms and plankton were collected during extensive sampling surveys undertaken in the Irish Sea on-board the RV *Prince Madog* in June 2014 from the locations shown in Fig. 3.1. Sampling station details are presented in Table 3.1. Sampling was undertaken in the north- east Irish Sea east basin (station EB2) at *ca.* 28 m depth; and in the west basin (station WB) at *ca.* 133 m depth. Commercially important fish, molluscs and crustacean samples were collected from nine Irish Sea stations (Table 3.1) during fish stock surveys (cruise no. CO4114) conducted on-board the RV *Corystes* by the Agri-Food and Biosciences Institute, Northern Ireland (AFBI-NI) during October 2014 (Fig. 3.1). The on-board ship sampling procedure and laboratory treatment are described separately for each sample type below.

Table 3.1. Sampling station details for the Irish Sea

Sampling station	Date sampled	Station co-ordinates	Sample type(s)
EB2	10 June 2014	54 28.00 N, 03 44.00 W	seawater, sediment, plankton, benthic organisms
WB	11 June 2014	54 13.00 N, 05 04.00 W	seawater, sediment, plankton, benthic organisms
86	20 October 2014	54 35.68 N, 05 26.30 W	fish survey
208	09 October 2014	53 48.84 N, 05 46.40 W	fish survey
257	13 October 2014	54 24.44 N, 03 45.77 W	fish survey
259	13 October 2014	54 16.83 N, 03 42.84 W	fish survey
242	08 October 2014	54 06.04 N, 04 02.39 W	fish survey
342	08 October 2014	53 55.32 N, 03 49.82 W	fish survey
245	08 October 2014	53 30.12 N, 04 11.20 W	fish survey
Area G	16 February 2015	54 20.44 N, 05 24.38 W	scallop survey
Area H	16 February 2015	54 08.72 N, 05 44.17 W	scallop survey

3.2.1.1 Seawater biogeochemical carbon fractions

Surface water samples (*ca.* 2 m depth) were obtained for stations EB2 and WB by pumping 160 l of seawater on-board with an electric pump into pre-washed 20 l containers for subsequent ^{14}C analysis of DIC, DOC, PIC and, POC fractions. Each container was rinsed with seawater prior to complete filling. Each 20 l sample was filtered immediately on-board using pre-furnaced (400^{o}C) 150 mm diameter GF/F (Whatman) glass fibre filters, within a positive pressure N_2 filtration system. GF/F filters have the smallest available pore size (0.7 μm) suitable for ^{14}C analysis (to avoid extraneous carbon contamination) and therefore define 'dissolved' and 'particulate' material in this study. Particulate material from 40 l of seawater was collected on each filter, wrapped in aluminium foil and stored at −20^{o}C prior to ^{14}C analysis. Several 500 ml aliquots of filtrate were collected for DIC analysis in 1 l foil bags (FlexFoil PLUS, SKC Inc., USA). Again, these were rinsed with filtered seawater, re-filled and stored at −20^{o}C. Separate 500 ml aliquots of seawater were collected for DOC analysis. These were transferred into cleaned, pre-furnaced (500^{o}C) and pre-rinsed glass bottles which were then re-filled and acidified with (85%) orthophosphoric acid to liberate DIC from the sample (Burr *et al*., 2001), thus halting photosynthetic processes and fixing the organic carbon content. Bottles were refrigerated at 3^{o}C on-board. All analyses of the biogeochemical fractions were undertaken at the SUERC ^{14}C laboratory.

PIC/POC

Filter papers containing particulate material from either 40 or 80 l of seawater (depending on the PIC concentration of the seawater) were placed within a reaction vessel under vacuum. Carbon dioxide (CO_2) was generated by acid hydrolysis of PIC material held on the filters using 50 ml of 1M HCl and subsequently cryogenically trapped and purified prior to ^{14}C analysis. Acidified GF/F filters were retained for ^{14}C analysis of POC material. These were thoroughly washed over a clean GF/F filter paper using ultra-pure water (using vacuum filtration) to remove any traces of acid and subsequently oven dried at 40^{o}C. Both filters were transferred into quartz tubes for subsequent sealed-tube combustions to liberate CO_2 (section 2.1.5) (Vandeputte *et al*., 1996). The CO_2 was again cryogenically purified for subsequent conversion to graphite and analysis by accelerator mass spectrometry.

DIC

Seawater samples (500 ml) contained in foil bags were thawed in a refrigerator and transferred under vacuum to a reaction vessel. Complete acid hydrolysis of the seawater was performed for each sample by introducing two aliquots of *ca.* 10 ml (85%) orthophosphoric acid to the vessel. Helium gas was passed through the sample/ acid mixture at positive pressure to evolve the CO_2, according to the method of Bryant *et al*. (2013). CO_2 was isolated and cryogenically purified using the regime described in section 2.1.5 in preparation for graphitisation and AMS measurement.

DOC

Representative DOC concentrations were obtained for Irish Sea water samples by using high-temperature combustion of dried salts (and adhering dissolved organic matter) according to the method of Fry *et al*. (1996). Some modifications were made to the method and are briefly described as follows. For each station (EB2 and WB), pre-acidified (orthophosphoric acid) seawater aliquots (500 ml) were transferred to a 1.5 l pre-furnaced (600^{o}C) high purity quartz glass vessel. Water samples were evaporated to dryness under vacuum according to the method described in Burr *et al*. (2001). Using this method, samples are never exposed to the atmosphere. The DIC component is removed during drying and the resulting salt contained within the vessel is detached from the evaporation apparatus and transferred to a separate vacuum rig for combustion. The samples, including salts, were combusted at 850^{o}C for >2.5 hrs, where the sulphate contained in the salt provided the oxidant for the organic matter (Fry *et al*., 1996).

Liberated gases were passed through a series of traps: ethanol/ dry ice (−78°C) to remove water vapour, pentane/ liquid nitrogen (−130°C) to remove SO_2 and the remaining gases (including CO_2) collected using liquid nitrogen (−196°C). The sample gas, collected using liquid nitrogen, underwent a secondary (closed) combustion at 850°C (>3hrs) with 2g MnO_2 and 2g CuO added to the vessel to remove traces of HCl and SO_2, oxides of nitrogen and other contaminants. CO_2 samples were cryogenically purified for subsequent conversion to graphite and AMS measurement.

3.2.1.2 Sediment

Several sediment cores were obtained from each sampling site using an OSIL Maxi-Corer with 600 kg weight and 8 core boxes, with 600 mm length × 110 mm diameter polycarbonate cores for each. Sediment cores recovered at each deployment were ca. 30 – 40 cm in length and were immediately extruded and sectioned on-board into 1 cm vertical depth increments. Samples were labelled, bagged and frozen (−20°C) pending analysis at SUERC.

Core sections were thawed at 3°C and the outer (approx.) 1mm was discarded to avoid the effects of smearing during extrusion. Samples were weighed, oven-dried at 40°C and reweighed to obtain a wet: dry mass ratio and finally they were gently ground into a fine powder using a mortar and pestle. Organic ^{14}C analysis was undertaken on three samples from single cores selected from stations EB2 and WB, representing the sediment core surface, middle and base horizons. In each instance, the samples were acid-washed with 1M HCl to remove the carbonate component, rinsed in deionised water, and oven-dried (40°C) prior to sealed combustion at 850°C (Vandeputte *et al*., 1996), CO_2 purification, graphitisation and AMS ^{14}C analysis. Approximately 100 – 500 mg of sediment was combusted, depending on the organic content of each sample.

3.2.1.3 Marine biota

Benthic biota were sampled at each station (EB2 and WB) by two 15 minute trawl deployments using a 2 m beam trawl, yielding a wide diversity of organisms at each site (supplementary Table A.1). Additionally, several deployments were made using a Van Veen grab and Day grab to collect infaunal species. At each site, several specimens of each species were selected (where available) to enable multiple sample ^{14}C analyses to

be performed. Specimens were washed in seawater over a sieve, formally identified and immediately frozen, pending transport to the laboratory. Samples collected from fish stock surveys by AFBI-NI; (supplementary Table A.2) were also immediately frozen after collection and transported to SUERC for ^{14}C analyses.

Samples were thawed in a refrigerator overnight and washed thoroughly with high purity water to remove adhering sediment and debris. Muscle tissue or soft tissue was sub-sampled from each specimen for ^{14}C analysis, to provide contemporary information on ^{14}C uptake in biota relative to the carbon turnover time in each species. Bones and carapaces were not analysed. Tissue sub-samples were weighed and freeze-dried, then re-weighed for wet:dry ratio calculation. Where more than one individual of a species was collected, dried tissue samples were proportionally combined (with the same mass taken from each individual). Multiple samples were made where six or more individuals of a species were available. Small individuals e.g. polychaetes, or analogously similar species e.g. crabs or starfish (inhabiting similar niches) were combined into their higher classification groups. Approximately 10 – 15 mg of each sample was weighed from each species and combusted using the sealed quartz tube combustion method to liberate CO_2.

3.2.1.4 Plankton samples

Plankton samples were collected from each station by deployment of plankton nets. Nets were deployed to the maximum depth at each station then hauled to the surface. Samples were rinsed into the sieve capsule and separated into fractions of > 270 μm mesh size for zooplankton and 80 – 270 μm mesh size for phytoplankton samples. Specimens were transferred into containers and frozen on-board at −20ºC.

Immediately prior to analysis, specimens were thawed at room temperature, thoroughly washed with deionised water, freeze dried and ca. 10 – 15 mg of each sample were weighed and combusted using the sealed quartz tube combustion method to produce CO_2 for subsequent graphitisation and AMS measurement.

3.2.2 ^{14}C analysis

For all samples collected, carbon dioxide was liberated either by sealed quartz tube combustion (for organic material) or by acid hydrolysis (for DIC and PIC), cryogenically

purified under vacuum with dry ice-ethanol and liquid N_2 traps, and 3 ml subsamples of CO_2 converted to graphite according to the procedure of Slota *et al*. (1987). Sample $^{14}C/^{13}C$ isotope ratios were measured on the SUERC 250kV SSAMS or the 5 MV tandem AMS (Freeman *et al*., 2008, 2010) and with quality assurance standards described in Naysmith *et al*. (2011) and Dunbar *et al*. (2016). Stable isotope ($\delta^{13}C$) ratios were measured offline on a VG SIRA 11 isotope ratio mass spectrometer. ^{14}C results were calculated relative to the international standard (oxalic acid II, SRM-4990C) as ^{14}C activity ratios (fraction modern, $F^{14}C$). Fraction modern results were converted to specific activities (Bq kg^{-1} C) using the regime for calculating enhanced activity samples described by Mook and van der Plicht (1999). Uncertainties are typically less than 0.5% of the measured activity for AMS, and have been omitted from figures for clarity.

3.3. Results and Discussion

3.3.1 ^{14}C in biogeochemical carbon fractions of seawater

The liquid ^{14}C discharge for June 2014 (24.7 GBq) was an order of magnitude less than preceding monthly discharges for 2014 (January to May) which ranged from 201 to 828 GBq, and the lowest monthly ^{14}C discharge since April 2001. Monthly discharges from January 2012 – December 2014, the period encompassing and immediately preceding this study, are given in Figure 3.3. ^{14}C discharges from January 2012 onwards show large seasonal fluctuations, with peak discharges occurring during the winter months (November to February), coinciding with the periods of limited primary production in the Irish Sea, and reduced discharges in the spring and summer months (May – August). Nevertheless, the gross DIC activity (546 ± 2 Bq kg^{-1} C) at station EB2, collected in June 2014, (Table 3.2) is more than twice the level of ambient background. However, it is difficult to ascertain whether this enhancement is contemporary with June 2014 discharges only, or contains a residual component of DIC from preceding higher monthly discharges retained in the water column. The $\delta^{13}C$ values in the DIC (and PIC) fractions are within the range for marine inorganic carbon (−1.0 to + 1.0‰ relative to VPDB), indicating that there is no significant terrestrial influence on these fractions during sampling. The $\delta^{13}C$ value for the POC fraction (−21.9‰) is commensurate with $\delta^{13}C$ values for Irish Sea suspended particulate organic matter of between −18.0 and −22.0‰ (MacKenzie *et al*., 2004), compared with terrestrially-derived organic matter of between −24.0 and −32.0‰ (Gulliver, 2002), and demonstrates that the POC at station EB2 is

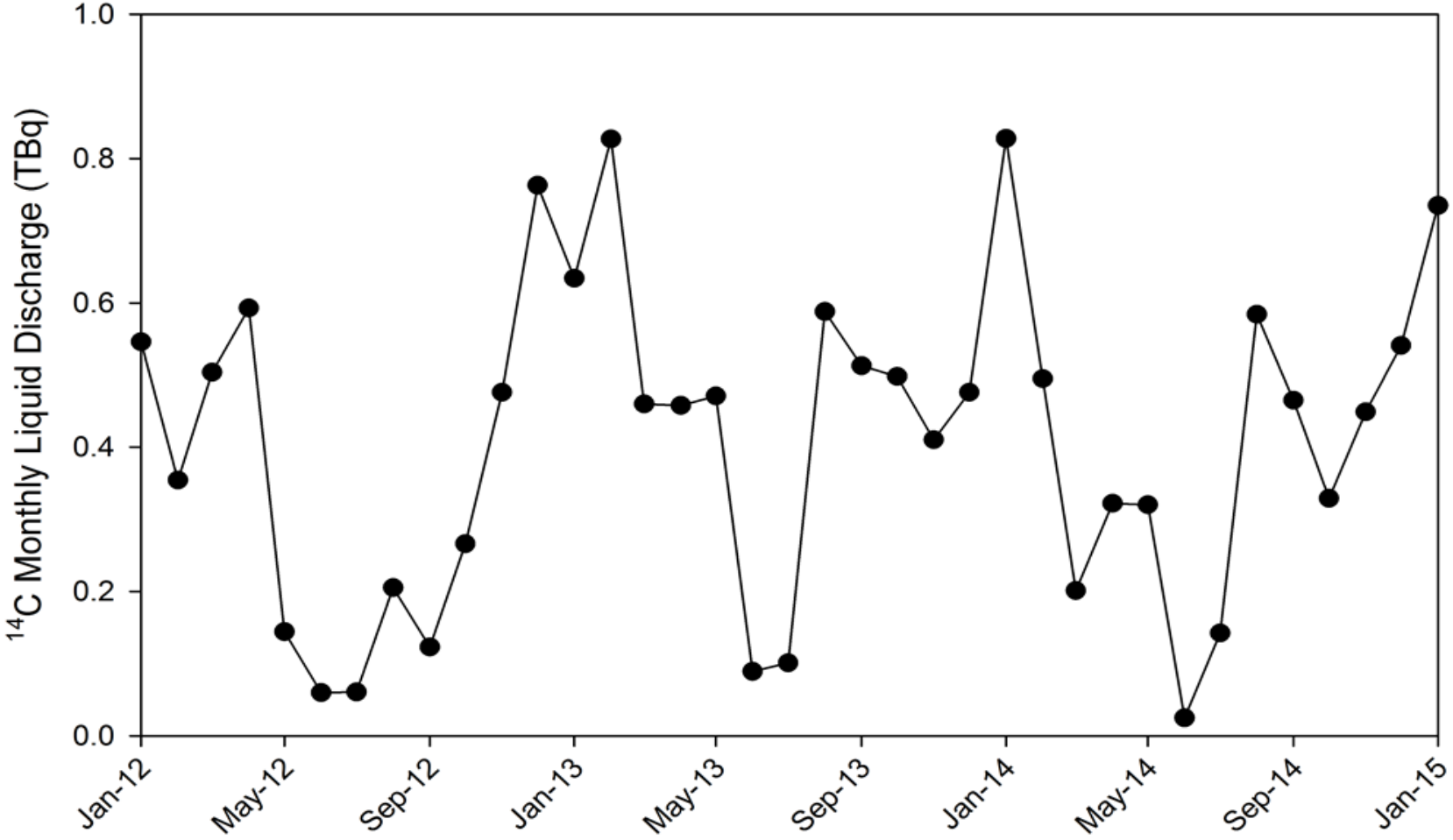

Figure 3.3. Monthly liquid ^{14}C discharges from Sellafield (TBq) since January 2012. (Sellafield Ltd., 2015).

predominantly of marine origin. The gross activity in the POC fraction (471 ± 2 Bq kg^{-1} C) is lower in activity than the DIC fraction but still enriched, confirming that POC is derived largely from the DIC reservoir. Whilst ^{14}C enhancements observed in the DIC and POC fractions are only a 'snapshot' of ^{14}C activities overlying station EB2, they provide convincing evidence for the mechanistic transfer from dissolved ^{14}C to particulate organic material. The PIC fraction is slightly depleted at station EB2 (244 ± 1 Bq kg^{-1} C). Transfer from DIC to PIC occurs mainly through uptake by molluscs and other calcareous organisms during shell formation. No calcareous foraminiferans were observed on the PIC/POC filter papers when viewed under a microscope and as such, demonstrate their low prevalence in the eastern basin during sampling. Therefore, the main process is likely to be gradual erosion of larger shells in the intertidal zone as described in Cook *et al*. (2004), Muir *et al*. (2015) and Tierney *et al*. (2016). This process will occur slowly and will be small when compared to inputs from sedimentary/substrate sources of which old material represents a significant fraction of the carbonate in this system (MacKenzie *et al*., 2004). The $\delta^{13}C$ value (−30.3‰) for the DOC sample denotes material derived from a terrestrial organic source, possibly originating from (^{14}C depleted) riverine runoff from the Cumbrian coast. Consequently, the ^{14}C activity is significantly depleted in the DOC fraction at station EB2 (88 ± 1 Bq kg^{-1} C).

The DIC and POC fractions at station WB are slightly enhanced and of comparable ^{14}C activity, supporting the transfer mechanism of ^{14}C from the DIC to the POC reservoir, predominantly through uptake by phytoplankton, but also by inputs from the non-living components of POC such as faecal matter and other organic detritus. $\delta^{13}C$ values in DIC, PIC and POC fractions are consistent with material predominantly of marine origin. The ^{14}C activity uniformity observed between the DIC and POC reservoirs indicates that the western Irish Sea is receiving relatively homogenous ^{14}C inputs from the eastern Irish Sea, and would therefore be subject to the same transfer mechanisms discussed above. The PIC fraction at station WB is depleted in ^{14}C, and similarly to PIC at station EB2, the transfer process from DIC to PIC will be slow and strongly influenced by the presence of a significant pool of old carbonate material. DOC is depleted at station WB, suggesting that the carbon is from an 'old' source of possibly re-cycled DOC material. Unfortunately, there was insufficient carbon present in the sample to perform stable carbon isotope analysis to determine if this material was influenced by terrestrial runoff.

Table 3.2. Gross and net specific ^{14}C activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ (‰ relative to VPDB) values from the four ^{14}C biogeochemical fractions of Irish Sea water samples. Net activities above the ambient background of 249 ± 1 Bq kg^{-1} C are in bold. Samples with values lower than this are marked as 'Depleted'.

Location	^{14}C specific activities (Bq kg^{-1} C ± 1σ) $\delta^{13}C$ (‰)			
	DIC	PIC	DOC	POC
Station EB2	546 ± 2 **297 ± 2** (−0.7‰)	244 ± 1 **Depleted** (+1.0‰)	88 ± 1 **Depleted** (−30.3‰)	471 ± 2 **222 ± 2** (−21.9‰)
Station WB	264 ± 1 **15 ± 1** (+1.0‰)	214 ± 1 **Depleted** (+1.1‰)	77 ± 1 **Depleted** (na)*	259 ± 1 **10 ± 1** (−20.0‰)

* na: insufficient carbon in sample for $\delta^{13}C$ (‰) analysis

3.3.2 Sediment

^{14}C activities in the organic component of surface sediment (0-1 cm) for stations EB2 and WB are presented in Table 3.3. Station EB2 shows ^{14}C enhancements at all depth horizons, indicative of Sellafield ^{14}C inputs. $\delta^{13}C$ values indicate that the organic material is largely of marine origin but with evidence of a small terrestrially-derived input distributed evenly throughout the core. The relative uniformity in ^{14}C enhancement throughout the core and consistency of $\delta^{13}C$ values, suggests that the sediment is subject to intense bioturbation and homogenisation throughout its complete depth, in agreement with the findings of other studies (e.g. Kershaw, 1986; Kershaw *et al*., 1983, 1984, 1999; MacKenzie and Scott, 1993; MacKenzie *et al*., 1998). The surface sediment is depleted in ^{14}C relative to the POC in the overlying seawater, and is contrary to what might be expected in the north-east Irish Sea given the continuous nature of ^{14}C inputs and transfer processes to the POC fraction. This activity disparity may have resulted from the loss of enriched surface material during core collection, although the *Maxi-Corer* was deployed to prevent such losses, and no significant resuspension of material was seen during core recovery or during the core sectioning process. In the latter case, sectioning at 1 cm increments would effectively dilute enriched sediment with 'older' organic material if the enriched material is confined only to the uppermost sediment surface. It is reasonable to assume however, that the principal mechanisms for this activity difference arise from the attenuation of the ^{14}C enriched POC arriving at the sediment surface, through rapid

physical mixing, bioturbation and incorporation of POC into sediment dominated by older organic material. To explore this possibility, a single ^{14}C analysis was undertaken on the less dense fraction of the surface sediment from station EB2 (0-1 cm), obtained from the bulk sediment using a settling method (Poppe *et al*., 2001), and assumed to contain organic particles (and clay minerals). A low temperature (< 400ºC) combustion was then undertaken to minimise the contribution of 'old' clay-bound carbon (McGeechin *et al*., 2001). The ^{14}C analysis revealed that this fraction had an activity of 413 Bq kg^{-1} C ($\delta^{13}C = -20.8$) which is significantly enriched compared to the bulk surface sediment reported in Table 3.3, and more comparable to the POC fraction (471 Bq kg^{-1} C) at station EB2, demonstrating that the mixing processes at the sediment surface can account, at least in part, for the anomalously low sediment activities relative to the biota. This has implications both for biotic uptake of ^{14}C, depending on the degree of degradation of organic matter in this fraction, and remobilisation processes from sediments and is the subject of ongoing research. Further build-up of enriched POC in sediments may be prevented by benthic organisms rapidly scavenging labile (^{14}C enhanced) organic matter prior to, or immediately after incorporation into sediments or from oxidative loss (and/or tidal dispersal) of organic material to the water column.

Table 3.3. Sediment organic fraction gross and net ^{14}C activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ values (‰ relative to VPDB) in surface, middle and base horizons for stations EB2 and WB. Net activities are in bold. Values lower than ambient background (249 ± 1 Bq kg^{-1} C) are denoted as 'Depleted'.

Horizon depth (cm)	**Sediment Core**			
	Station EB2		**Station WB**	
	^{14}C activity (Bq kg^{-1} C)	$\delta^{13}C$ (‰)	^{14}C activity (Bq kg^{-1} C)	$\delta^{13}C$ (‰)
0-1 (surface)	298 ± 1 **49 ± 1**	−23.0	170 ± 1 **Depleted**	−21.9
15-16	295 ± 1 **46 ± 1**	−23.2	152 ± 1 **Depleted**	−21.9
29-30 (station EB2 base)	264 ± 1 **15 ± 1**	−23.0	- -	- -
34-35 (station WB base)	- -	- -	155 ± 1 **Depleted**	−21.5

Station WB is depleted in ^{14}C, relative to ambient background, and does not show any evidence of a Sellafield-derived ^{14}C contribution to the sediment. Kershaw *et al*. (1999) noted that sediments in the west basin are subject to intense physical mixing processes, either by bioturbation and/or fishing and the contribution of Sellafield-derived ^{14}C may be insufficient to cause enrichment of surface sediments. The uniformity in ^{14}C activities and the $\delta^{13}C$ profile at station WB could suggest that ^{14}C enhanced material might be rapidly consumed and/or re-worked and homogenised throughout the sediment. $\delta^{13}C$ values at station WB are higher than at station EB2, indicating a higher contribution of marine organic material at station WB compared to that of station EB2.

3.3.3 ^{14}C in north-east Irish Sea benthic and planktonic organisms: station EB2

The results from biota collected in June 2014 are presented in Figure 3.4. Supplementary Table A.1 details the number of individuals analysed, the average species size and size range (fish only), and the gross specific ^{14}C activities (Bq kg^{-1} C) for each species. All benthic organisms show ^{14}C enhancements above ambient background, indicative of a supply of enriched ^{14}C to this site. Epifaunal or infaunal organisms feeding on or within sediment respectively, have higher ^{14}C values than those feeding from the water column. Phytoplankton, zooplankton and suspension feeders *e.g.* the soft coral (*Alcyonium digitatum*) and dahlia anemone (*Urticina felina*) have the lowest ^{14}C activities amongst the macrobenthos and have ^{14}C activities broadly consistent with the seawater DIC and POC fractions at the time of sampling. Large inter-species variations are apparent at station EB2 and intra-species variation is also evident in dab (*Limanda limanda*) samples 1 and 2. ^{14}C activity variations are discussed here in relation to species-specific ecology and feeding habits. For the purpose of this study, individual samples of infaunal or epifaunal invertebrates (crabs, starfish and polychaetes) were combined into their higher taxonomic groups and are described in these terms.

The gross phytoplankton ^{14}C activity (520 Bq kg^{-1} C) is similar, at the time of sampling, to the gross DIC ^{14}C activity (546 Bq kg^{-1} C) of seawater. The gross ^{14}C activity of the zooplankton (458 Bq kg^{-1} C) is similar to the POC activity at station EB2 (471 Bq kg^{-1} C), but lower than their principal food phytoplankton (520 Bq kg^{-1}). Zooplankton samples at station EB2 were dominated by copepods which feed exclusively on phytoplankton. Nevertheless, zooplankton will be integrating carbon over a longer period of time than phytoplankton, which has a relatively fast carbon turnover rate and will

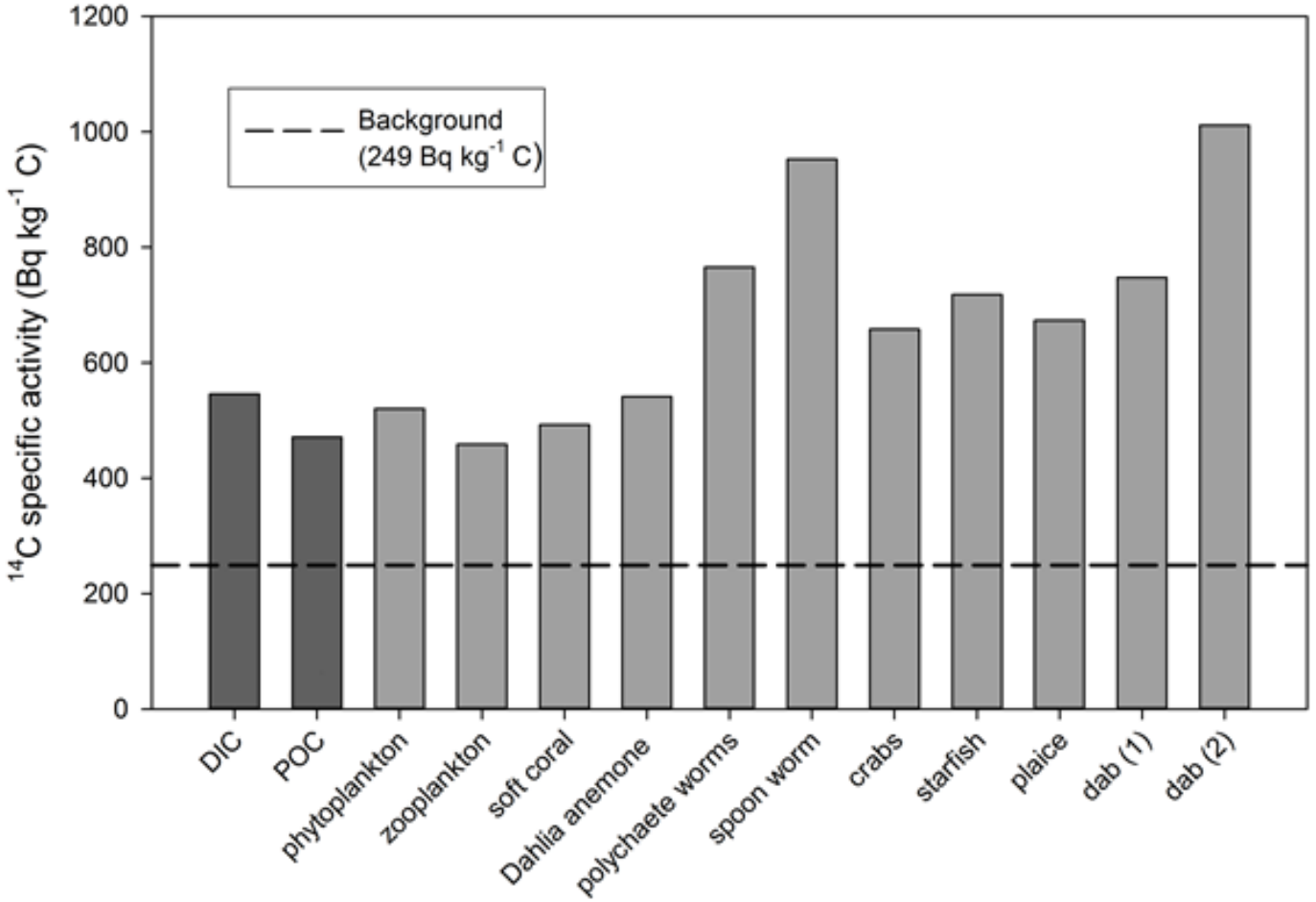

Figure 3.4. Gross specific ^{14}C activities (Bq kg^{-1} C) in benthic organisms and DIC/POC seawater biogeochemical fractions collected at station EB2. The dashed line indicates the measured background activity of 249 Bq kg^{-1} C measured in *Mytilus edulis* (blue mussel) shells obtained from the West Coast of Ireland.

readily 'capture' transient ^{14}C enhancements in DIC from the water column. Seawater samples were collected from the surface (2 m depth) while plankton samples were collected from the whole water column, and any depth/ ^{14}C activity stratification would influence overall plankton activities. The apparent activity disparity between zooplankton and phytoplankton underlines the spatial and temporal variability of ^{14}C uptake in planktonic organisms.

Soft coral is a passive suspension feeder on both phytoplankton and zooplankton (Roushdy and Hansen, 1961; Fabricius *et al*., 1995) and although feeding preferentially on zooplankton, soft coral shows trophic opportunism in its feeding habits (Migne and Davoult, 2002). The soft coral ^{14}C activity (492 Bq kg^{-1} C) lies between the end members of its immediate food sources of zooplankton and phytoplankton at 458 and 520 Bq kg^{-1} C, respectively, and is in good agreement with the mean planktonic ^{14}C activity of 489 Bq kg^{-1} C. The dahlia anemone (*Urticina felina*) is a carnivorous feeder, typically consuming small fish, crustaceans, molluscs, shrimps, and urchins. The ^{14}C activity of this species (542 ± 3 Bq kg^{-1}) is more akin to that of planktonic species in the east basin, indicating that it is deriving the majority of its food from a lower ^{14}C activity source, quite possibly from planktonic crustaceans (Rasmussen, 1973) and to a lesser extent from other benthic biota. The comparable ^{14}C activities of the soft coral and dahlia anemone with that of plankton suggest that these organisms are principally feeding from the water column. However, both these species are long-lived with the life-span of the dahlia anemone exceeding 50 years (Jackson and Hiscock 2008) and the soft coral exceeding 20 years (Hartnoll, 1998), demonstrating that they will integrate ^{14}C over a much longer period than comparably short-lived plankton.

A specific activity increase of >285 Bq kg^{-1} C is observed between the mean ^{14}C activity of planktonic species and those organisms feeding from the water column to that of benthic organisms occupying higher trophic levels at station EB2, implying that these groups are reasonably distinct in their carbon sources. This also presents an activity paradox between the higher ^{14}C activities observed in (non-suspension feeding) benthic organisms and the relatively low ^{14}C activities observed in sediment, planktonic organisms and seawater biogeochemical fractions. The ecology of these benthic organisms is discussed in relation to species-specific ^{14}C measurements.

Infaunal invertebrates, living either partly or wholly within sediment, are dominated at station EB2 by polychaete worms, which form the largest and most diverse community in soft subtidal sediment. Polychaetes may be carnivorous but may also consume algal matter. Many burrowing species or tube dwellers are deposit feeders that consume directly any organic particles from sand or mud, or extend tentacle-like structures to the sediment surface and convey detritus to the mouth (Lalli and Parsons, 1993). Crabs are predominantly omnivorous predator/ scavengers and deposit-feeders, whereas starfish prey upon a wide range of living organisms and carrion that include molluscs, polychaete worms and other echinoderms, small crustaceans, anemones and carrion, which may reflect their higher ^{14}C activity. The spoon-worm (*Maxmuelleria lankesteri*) was analysed separately for ^{14}C, as this species forms a major component of the burrowing megafauna of the north-east Irish Sea and is postulated to significantly affect the distribution of radionuclides in bottom sediments (Hughes *et al*., 1996 a,b; Kershaw *et al*., 1983, 1984, 1999). The spoon-worm is found at high densities in the Irish Sea (up to 35 m^{-2}) (Williams *et al*., 1981; Swift, 1993) and is a sedentary deposit feeder of sediment which it obtains by extending its proboscis from the burrow to graze the accessible sediment surface (Hughes *et al*., 1993, 1994). The ^{14}C activity (953 Bq kg^{-1} C) infers that spoon-worms are selectively feeding on a ^{14}C enhanced carbon source arriving at the surface sediment. Rapid scavenging (and bioturbation) caused by spoon-worms, polychaetes and other benthic detrivores of ^{14}C enhanced organic material is, therefore, likely to be a significant reason for the depleted activities measured in organic sediments.

North-east Irish Sea plaice preferentially consume polychaetes (*Nephtys* spp.) and bivalves (*Abra alba*) (Johnson *et al*., 2015). The ^{14}C activity of plaice (673 Bq kg^{-1} C) is of the same order as crab, starfish and dab (sample 1), indicating that these species are consuming organisms with broadly similar ^{14}C activities. In contrast to plaice, dab have a wide-ranging diet of larger and more energy-rich prey, primarily favouring crustaceans e.g. mud-shrimps (*Callianassa subterranea* and *Jaxea nocturna*) and angular crab (*Goneplax rhomboides*) (Johnson *et al*., 2015). This could explain their relative enhancement over plaice, although the former two prey species were not obtained at station EB2 and therefore, it was not possible to test this assertion. The highest ^{14}C activity was recorded for dab (2) at 1012 Bq kg^{-1} C. It is unclear whether this enhancement is due to prey selection, one or more individuals feeding from an area that is highly enhanced in ^{14}C or if individuals in the lower activity sample (dab sample 1) are feeding in a ^{14}C depleted area. Age and size differences between individuals may

influence both dietary preference and ^{14}C activity, however, the relatively narrow size range observed between dab individuals (80−130 mm; average 110 mm) tends to preclude this argument. Whilst predator-prey interaction could explain some ^{14}C enhancement observed in benthic species occupying higher trophic levels, it does not explain fully the increase noted between planktonic/ suspension feeding organisms and higher trophic level organisms. The integration period over which an organism has consumed ^{14}C-enriched material and the carbon turnover rate within each organism are factors that will influence the overall species activity. The lower ^{14}C activity observed in plankton is due to their fast carbon turnover rate and, as such, is representative of the relatively low ^{14}C discharges occurring from Sellafield immediately before or during the sampling period (June 2014). The higher ^{14}C activities observed in higher organisms suggest that they are integrating ^{14}C over a longer time period, coinciding with periods of higher ^{14}C discharge.

3.3.4 ^{14}C in north-west Irish Sea benthic and planktonic organisms: station WB

In contrast to the heterogeneity observed at station EB2, most benthic biota at station WB show small ^{14}C enhancements above ambient background (Figure 3.5). Supplementary Table A.1 details the number of individuals analysed for ^{14}C and the gross specific ^{14}C activities for each species. Phytoplankton and zooplankton have the lowest ^{14}C activities at 242 and 254 Bq kg^{-1} C, respectively, comparable with DIC (264 Bq kg^{-1} C) and POC (259 Bq kg^{-1} C) activities at the time of sampling. For most organisms, similarly to station EB2, ^{14}C activities exceed that of the surrounding sediment, planktonic organisms and seawater biogeochemical fractions. Dab, starfish (*Asteroidea* spp.), dragonet (*Callionymus lyra*) and the polychaete worm or 'sea mouse' (*Aphrodita aculeata*) are significantly enhanced in ^{14}C above the other organisms collected at station WB. The degree of enhancement in these species is analogous to, or exceeds ^{14}C activities in comparable organisms (e.g. dab, polychaete and starfish) at station EB2. ^{14}C activities are discussed in relation to the ecology of each species, while those organisms with significant ^{14}C enhancements are considered separately.

Phytoplankton is marginally depleted in ^{14}C (242 Bq kg^{-1} C) in comparison to the marine ambient background activity. This may be caused by the presence of a small fraction of old ^{14}C-depleted detrital material being retrieved from the water column during plankton sampling, effectively diluting the sample ^{14}C activity. Zooplankton show slight ^{14}C

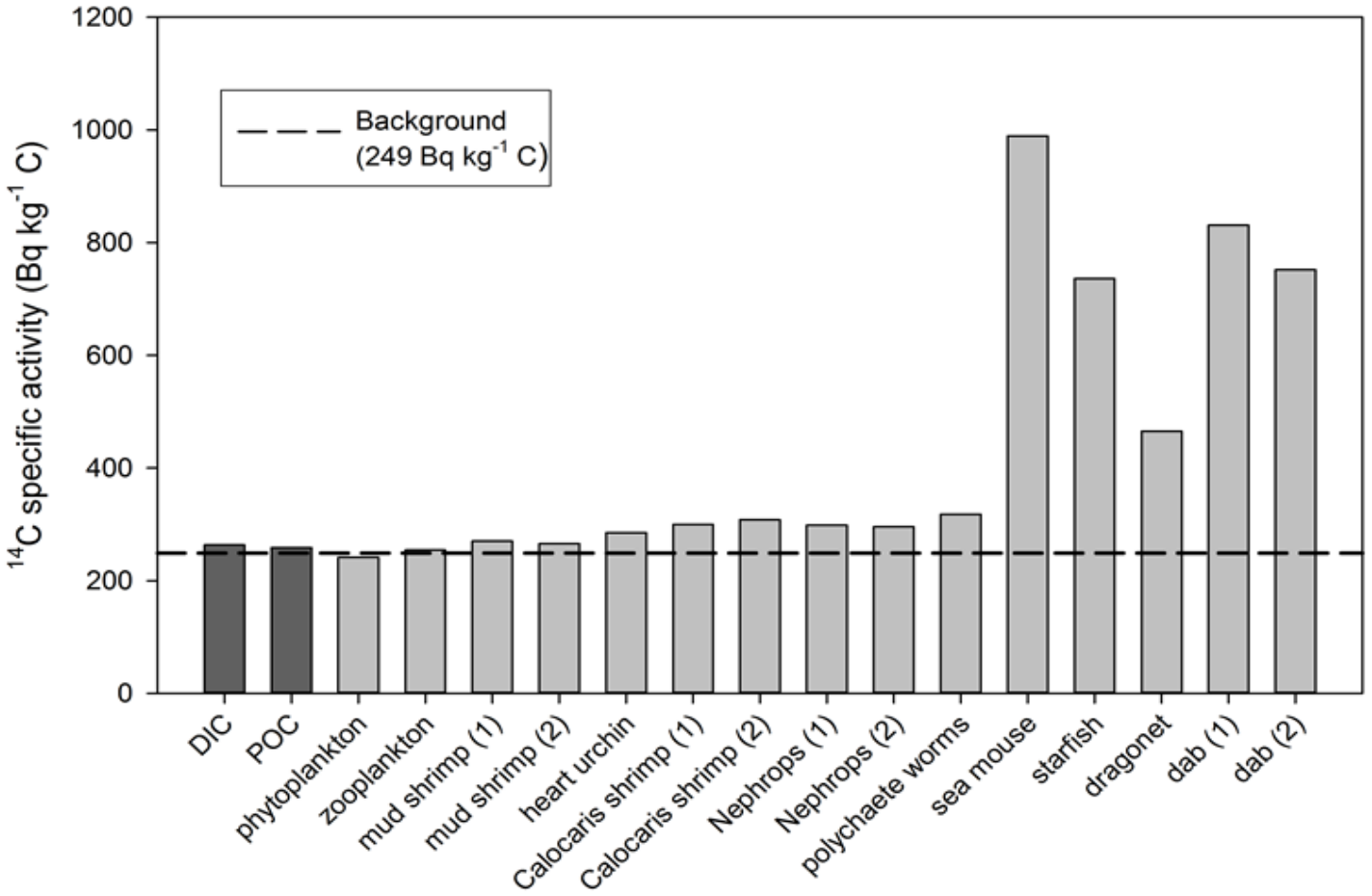

Figure 3.5. Gross specific ^{14}C activities (Bq kg^{-1} C) in benthic biota and DIC/ POC seawater biogeochemical fractions, collected at station WB. The dashed line indicates the measured background activity of 249 Bq kg^{-1} C, measured in *Mytilus edulis* (blue mussel) shells obtained from the West Coast of Ireland.

enrichment (254 Bq kg^{-1} C) reflecting recent time-integrated ^{14}C activities of phytoplankton (and DIC) in the western Irish Sea, and suggesting that the ^{14}C activity of (living) phytoplankton is probably enhanced. Mud-shrimp (*Callianassa subterranea*) have the lowest ^{14}C activity amongst all benthic organisms (mean 268 Bq kg^{-1} C). Mud-shrimp is a sub-surface deposit feeder that can supplement its diet from suspension feeding (Nickell and Atkinson, 1995). Suspension feeders at station EB2 also had notably lower ^{14}C activities, and could explain the limited ^{14}C enhancement in mud-shrimp. In comparison, a second species of mud-shrimp (*Calocaris macandreae*) has a mean ^{14}C activity of 304 Bq kg^{-1} C. *Calocaris macandreae* has several feeding strategies depending upon food availability including filter-feeding, scavenging and predation (Calderon-Perez, 1981), and these would influence the overall ^{14}C activity of this species. *Nephrops* is an opportunistic predator feeding on crustaceans, including *C. macandreae* (Smith, 1988), molluscs, and to a lesser extent polychaetes and echinoderms. The ^{14}C activity of *Nephrops* (297 Bq kg^{-1} C) is comparable to that of *C. macandreae* and its other prey species. Similarly to station EB2, polychaete worms are proportionally higher in ^{14}C activity (318 Bq kg^{-1} C) than other organisms. Nevertheless, the homogeneity of the system, in terms of ^{14}C activity, makes interpretation of ^{14}C uptake in most organisms difficult if based on feeding ecology.

Four species (including grouped starfish) show ^{14}C enhancements at station WB ranging from ca. $2 - 4$ times the ambient background level, which was unexpected given that station WB is approximately 130 km. (70 n.m) from the Sellafield discharge outfall. Interpretation is also problematic as it encompasses several species and both highly mobile (dab and dragonet) and slower-moving organisms (sea mouse and starfish). Dab are migratory, moving from shallow inshore water to deeper offshore areas, on a seasonal basis, especially as juveniles (Ortega Salas, 1988; Rijnsdorp *et al*., 1992). Therefore, they could feasibly migrate and feed in an area with enhanced ^{14}C activities. However, for less mobile species such as the sea mouse and starfish, the western basin gyre (section 3.3) could provide a mechanism for transfer and retention of enriched ^{14}C material at depth, facilitating a pathway for limited or species-specific ^{14}C uptake in benthic organisms. This possibility requires greater investigation. It is equally justifiable to question why other benthic organisms collected at the same site show no such enhancement.

Overall, ^{14}C activities in benthic organisms, both at station EB2 and WB, appear to be driven by a combination of mechanisms: i) the quantity, 'bioavailability' and ^{14}C activity

of organic matter supplied to sediments; ii) feeding behaviour: mobility, scavenging/ feeding proficiency and selectivity for ^{14}C-enriched organic material; iii) the assimilation and integration period for ^{14}C enriched food, and carbon turnover rate of each species; and iv) trophic-level transfers of ^{14}C through predator-prey interaction. Micro-, or even nano-scale processes could conceivably influence the transfer and uptake of ^{14}C in organisms, but were beyond the scope of this study.

3.3.5 ^{14}C in commercially important fish, molluscs and crustaceans

Results from samples obtained during fish and scallop stock surveys conducted by AFBI-NI are presented in Figure 3.6. Additional information detailing the number of individuals analysed for ^{14}C, the average species size and size range (fish only), and the gross specific ^{14}C activities for each species is given in supplementary Table A.2. Fish species can have complex movement patterns as well as diverse feeding behaviours. Consequently, the ^{14}C uptake mechanisms affecting these organisms will be driven by several factors including their proximity to, and time spent within feeding/ spawning grounds enriched in Sellafield-derived ^{14}C. Additionally, for migratory species such as the Atlantic herring (*Clupea harengus*) and Atlantic mackerel (*Scomber scombrus*), the location within and time spent transiting the Irish Sea will also be factors. ^{14}C uptake and removal will be affected by feeding behaviour, food availability/ source and subsequent transfer through the food chain via predator-prey interactions, as well as the carbon turnover rate of each species. ^{14}C activities in other commercially important species e.g. dab and plaice have been discussed in context with the 'ecosystem' ^{14}C activities observed at stations EB2 and WB (sections 3.3 and 3.4).

All Irish Sea organisms collected during the fish and scallop stock surveys have ^{14}C activities above the ambient background (Figure 3.6). Generally, higher ^{14}C activities can be observed in organisms from the eastern Irish Sea compared with those from the west, corresponding to their proximity to Sellafield. With the exception of the ^{14}C enhancements noted in station WB benthic organisms, western Irish Sea organisms are relatively uniform in ^{14}C activity in comparison to those found in the eastern Irish Sea, implying west basin organisms are foraging in a more homogeneous environment with respect to ^{14}C activity than those foraging in the east. Organisms such as the King scallop (Area G and H – west basin) whose main food source is phytoplankton and POC, and *Nephrops* (station 208 – west basin) have elevated ^{14}C activities compared with all fish

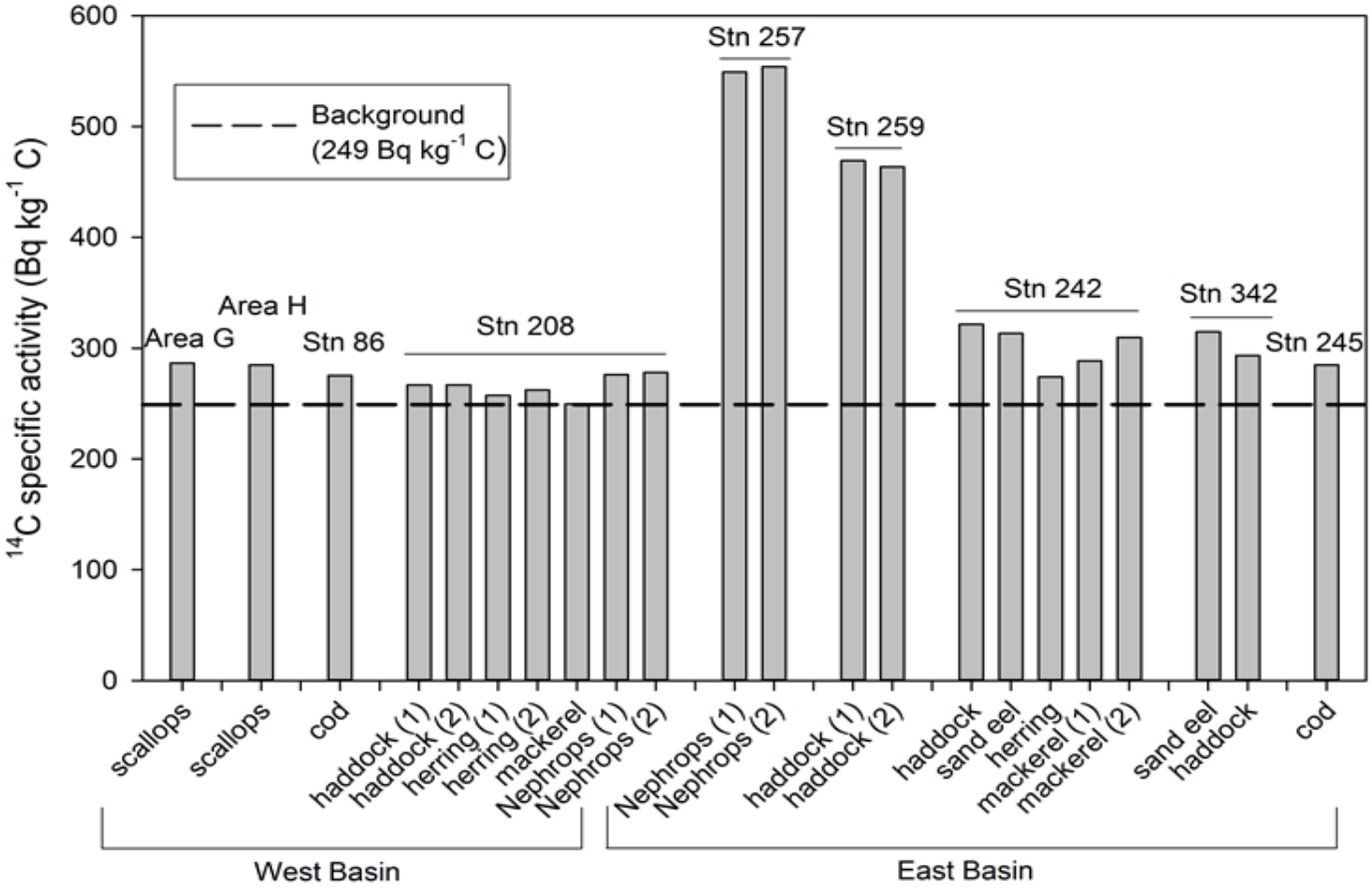

Figure 3.6. Gross specific ^{14}C activities (Bq kg^{-1} C) in commercially important Irish Sea fish, molluscs and crustaceans obtained during the fish and scallop stock surveys (conducted by AFBI-NI.). The dashed line indicates the measured background activity of 249 Bq kg^{-1} C, measured in *Mytilus edulis* (blue mussel) shells obtained from the West Coast of Ireland.

species in the west although scallops were collected later in the year than the other organisms. However, their enhancement indicates that their time-integrated food source is enriched in ^{14}C relative to that of fish, whose mobility allows foraging and feeding from relatively ^{14}C depleted areas. None of the western Irish Sea samples showed ^{14}C anomalous enrichment to the degree observed in station WB benthic organisms, from June 2014. Amongst the fish, cod (station 86 – west basin) and haddock (station 208 – west basin) have small ^{14}C enhancements over mackerel and herring at station 208 – west basin, possibly from feeding exclusively within the Irish Sea. Also, cod and haddock consume a number of species including *Nephrops* (Howard, 1989); mud-shrimps including *Calocaris macandreae* (Buchanan, 1963) and spoon-worms (Rachor and Bartel, 1981), and exhibit comparable ^{14}C activities to those species found at station WB. Herring are facultative zooplanktivorous filter-feeders (Blaxter, 1990), feeding mainly on copepods (Holst *et al*., 2004); whilst mackerel feed on small fish and crustaceans, crustacean larvae and other zooplankton (Collette and Nauen, 1983). In addition, the migratory nature of these fish, and consequent consumption of food outside the confines of the Irish Sea, will reduce their overall tissue ^{14}C activity and explain their near-background activity relative to enhanced activities found in other species at station 208.

A north to south decrease in ^{14}C activity is apparent in the eastern Irish Sea. *Nephrops* (station 257 – east basin) have the highest activity (mean: 552 Bq kg^{-1} C) corresponding to their close proximity to Sellafield (and to station EB2). Haddock were collected from three stations in the eastern Irish Sea (stations 259, 242 and 342 – east basin) and one from the west (station 208). ^{14}C activities reduce with distance from Sellafield implying that their foraging/feeding behaviour is area-specific, at least in the immediate months preceding sampling. The low ^{14}C activity in herring in the eastern Irish Sea is consistent with correspondingly low ^{14}C activities amongst their planktonic food source and so are possibly feeding in areas remote from Sellafield. Sandeel (*Ammodytes tobianus*) adults feed on zooplankton and some large diatoms (Bauchot, 1987) and their higher or comparable activity over other species at the east basin stations (242 and 342) may arise from more localised feeding as a result of a limited foraging range. Despite this, sandeel activity does not notably change between stations 242 and 342 (ca. 28 km (15 n.m.) apart) where the activity in haddock (a more mobile species) decreases. Mackerel samples 1 and 2 (station 242 – east basin) show intra-species variation (289 and 310 Bq kg^{-1} C respectively). Given the small amount of data it is difficult to conclude if this is due to one or more individuals feeding in an area of high activity or conversely, from a ^{14}C

depleted area. The size range for mackerel was narrow (220−240 mm; mean 230) and argues against age (and size), and hence dietary preference, influencing the ^{14}C activity differences in this species. However, the high mobility of mackerel, with a range extending beyond the Irish Sea may result in high ^{14}C variability.

3.3.6 Dose from ^{14}C to critical consumers of seafood from the Irish Sea

Dose rates (μSv) received by the critical consumers of seafood in the Irish Sea (Sellafield Fishing Community) are presented in Table 3.4 and, for comparison, the dose rate received from natural/ weapons testing ^{14}C inputs is included. Dose rates and the net ^{14}C activities were determined for the highest activities observed in commercially important species e.g. dab, plaice, haddock and *Nephrops* obtained for the NE Irish Sea. The average wet: dry weight ratios and percentage carbon content values for each species were used to convert ^{14}C activities from Bq kg^{-1} C to Bq kg^{-1} C fresh (wet) weight. The critical consumer group (Sellafield Fishing Community) 5-year average consumption rates (kg y^{-1}) were obtained from the CEFAS radiological habits survey (Garrod *et al*., 2015) of 14.8 kg y^{-1} cod, 31 kg y^{-1} other fish; 8.9 kg y^{-1} crabs, 6.9 kg y^{-1} lobsters; 12 kg y^{-1} other crustaceans; 7.4 kg y^{-1} winkles, 6.4 kg y^{-1} other molluscs. The dose per unit intake by ingestion of ^{14}C (5.8×10^{-10} Sv Bq^{-1}) was taken from ICRP–72 (ICRP, 1996). Most critical group species were not available from the north-east Irish Sea during sampling; therefore, dose calculations were based on 'worst-case' scenarios for consumption of commercial species with the highest observed ^{14}C activities in this study, e.g. dab, plaice, haddock and *Nephrops*. Total fish consumption (i.e. 45.6 kg) was calculated for 100 % consumption each of dab, plaice and haddock. For the crustaceans, 100 % (i.e. 27.8 kg) was assigned to *Nephrops*. Molluscs were omitted from the dose calculation.

The maximum dose from Sellafield-derived ^{14}C to the critical consumer group for this study (dab + *Nephrops*) of 2.05 μSv is in excellent agreement with the (mollusc subtracted) dose of 2.07 μSv (total dose: 2.8 μSv) reported by Sellafield in their 'summary of doses associated with marine discharges for 2014' (Nuclear Decommissioning Authority, 2015). The combined Sellafield and natural production/weapons testing dose of 2.90 μSv represents <0.3% of the annual permitted dose limit to a member of the general public.

Table 3.4. Dose rates (μSv) to the Sellafield Fishing Community critical consumer group of seafood from Sellafield-derived ^{14}C discharges and from natural/ weapons testing ^{14}C. 'Worst case' total dose scenarios are presented for critical consumers of fish and crustaceans with the highest ^{14}C activities observed in this study (dab, plaice, haddock and *Nephrops*).

Sample type/ station	Consumption rate (kg)	Average wet : dry ratio	Average % carbon	Dose from Sellafield ^{14}C (μSv)	Dose from natural/weapons testing ^{14}C (μSv)	Total Dose Sellafield and natural/weapons ^{14}C (μSv)
Dab (EB2)	45.8	4.8	39	1.67	0.54	2.21
Plaice (EB2)	45.8	4.4	42	1.07	0.63	1.69
Haddock (259)	45.8	4.6	43	0.54	0.62	1.16
Nephrops (257)	27.8	5.0	38	0.38	0.31	0.69
Total						
(Dab + *Nephrops*)	45.8 + 27.8	-	-	2.05	0.85	2.90
(Plaice + *Nephrops*)	45.8 + 27.8	-	-	1.45	0.94	2.38
(Haddock + *Nephrops*)	45.8 + 27.8	-	-	0.92	0.93	1.85

3.4. Conclusions

Highly variable ^{14}C activities across sediment, water and pelagic, demersal and benthic organisms indicate complex dispersal dynamics in the marine ecosystem of the Irish Sea, from initial discharge and transport as inorganic ^{14}C to subsequent biological uptake and transfer throughout the marine food chain. ^{14}C enhancements observed in the biogeochemical fractions of seawater and planktonic organisms substantiate a mechanistic transfer from the aqueous (dissolved) phase to the particulate phase, via DIC → plankton → POC, and that the constancy of supply and ^{14}C activity of plankton and POC are important factors in the transposition of ^{14}C to higher organisms.

In terms of ^{14}C incorporation into organisms, planktivorous species and those organisms predominantly feeding from the water column have markedly lower activities than benthic organisms occupying higher trophic levels at the east basin sampling station (EB2). Organism-specific ^{14}C uptake and transfer, dictated by feeding behaviour, the carbon integration period and turnover rate, as well as ensuing trophic-level transfer through predator-prey interactions are key concepts in this activity difference.

Notably, organic sediments, in which benthos live and feed located near to Sellafield show only modest ^{14}C enhancements over the total depth analysed (30 cm), and less than that of the benthic organisms found in surface sediments. It is proposed that the apparent 'loss' of enriched organic matter principally occurs through intensive physical mixing and bioturbation to depth of ^{14}C enriched organic material arriving at the sediment/ water interface, resulting in dilution with older organic material. Further build-up of ^{14}C in sediment would be limited through benthic organisms rapidly scavenging the more labile ^{14}C enriched organic material from surface sediments, and oxidative loss from the water column.

Most biotic and abiotic components of the ecosystem at station EB2 exhibit ^{14}C uptake and enrichment above ambient background. Whilst the degree of ^{14}C enrichment appears to be controlled by proximity to Sellafield, it is not exclusive to the eastern Irish Sea. Significant ^{14}C activities were observed in several western basin organisms, equal to, or in excess of ^{14}C activities observed in comparable east basin organisms. The western gyre is suggested as a possible mechanism for the ^{14}C transfer, retention and uptake in these organisms, but this remains, as yet, unconfirmed.

All Irish Sea pelagic and demersal fish have ^{14}C enhancements above background. Distinctions in ^{14}C activities in fish species can be made between those feeding in the eastern Irish Sea from those sampled in the west. Area-specific foraging/ feeding behaviour can be seen in some east basin species e.g. in haddock. The lowest ^{14}C activities are observed in planktivorous and migratory species.

This study demonstrates the pervasive nature of ^{14}C throughout the Irish Sea, coinciding with continuing nuclear re-processing activities and ^{14}C discharges from Sellafield. Nevertheless, it is important to restate that current Sellafield ^{14}C discharges contribute only a small dose to critical consumers of seafood from the Cumbrian coast. Dose rates presented here are comparable to those reported by Sellafield for 2014, and are negligible when compared with the annual UK dose limit of 1000 µSv to members of the public from all man-made sources of radiation (other than medical exposure); and the average annual (UK) dose received by an individual from natural sources of radioactivity (2230 µSv).

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Chapter 4
Ecosystem uptake and transfer of Sellafield-derived Radiocarbon (^{14}C)
Part 2: The West of Scotland

Abstract

Ecosystem uptake and transfer of Sellafield-derived radiocarbon (^{14}C) were examined within the West of Scotland marine environment. The dissolved inorganic carbon component of seawater, enriched in ^{14}C, is transported to the West of Scotland where it is transferred through the marine food web. Benthic and pelagic biota with variable life-spans living in the North Channel and Clyde Sea show comparable ^{14}C activities. This suggests that mixing of ^{14}C within the Irish Sea results in a relatively constant northwards dispersal of activity. Benthic species in the Firth of Lorn have similar ^{14}C enrichments, demonstrating that Irish Sea residual water is the dominant source to this area. Measured ^{14}C activities in biota show some similarity to western Irish Sea activities, indicating that dispersion to the West of Scotland is significant with respect to the fate of Sellafield ^{14}C releases. Activities measured in commercially important species do not pose any significant radiological risk.

This chapter has been published as:

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4.1 Introduction

4.1.1 Radiocarbon (^{14}C)

Radiocarbon (^{14}C) is estimated to be the largest contributor to the collective dose that the global population receives from the nuclear industry (UNSCEAR, 2008), due to its long half-life (5730 years) and ready uptake into the global carbon cycle. In the UK, the Sellafield nuclear fuel reprocessing facility is authorised to discharge waste ^{14}C to the atmosphere and the marine environment and this ^{14}C is the largest contributor to the collective dose commitment to UK and European populations from the entire nuclear industry (Nuclear Decommissioning Authority, 2015).

Atmospheric releases of ^{14}C from Sellafield largely dominated total discharges until 1994 when a change in discharge policy and, to a lesser extent, an increase in reprocessing activity resulted in increased marine ^{14}C discharges, which have continued since that time. The average marine ^{14}C discharge activity increased from < 2 TBq per year, between 1984 and 1993, to approximately 8 TBq per year since 1994 (BNFL, 1985-1989; MAFF, 1992-1995; RIFE, 1996-2014; Sellafield, 2015). Low-level radioactive effluent containing ^{14}C is discharged via pipelines that extend 2.1 km offshore into the Irish Sea. ^{14}C is released primarily as inorganic carbon and is incorporated into the dissolved inorganic carbon (DIC) component of seawater (Begg *et al*., 1991, 1992; Begg, 1992; Cook *et al*., 1995). Through fixation of inorganic carbon, marine photosynthesising organisms derive carbon from the DIC pool (Lalli and Parsons, 1993). Marine calcifying organisms, such as molluscs, also utilise DIC to build their exoskeletons (McConnaughey *et al*., 1997). These two pathways provide routes for the biological uptake of Sellafield-derived ^{14}C; however, it is the former that allows ^{14}C to be transferred throughout the entire food web.

Sellafield ^{14}C discharges are made in addition to existing "background" inputs of ^{14}C from natural production and fallout from atmospheric testing of nuclear weapons in the 1950s and early 1960s. Cook *et al*. (1998) and Tierney *et al*. (2016) presented near-identical background activities for the UK marine environment over 2 decades (248 ± 1.0 and 249 ± 0.8 Bq kg^{-1} C for the years 1995 and 2014, respectively). Therefore, marine background ^{14}C activity in this area is relatively stable and the latter value is used to define the modern ^{14}C background level in this study.

There have been various studies concerned with the fate of Sellafield-derived ^{14}C within the Irish Sea (e.g. Begg *et al*., 1992; Cook *et al*., 1995, 1998, 2004; Wolstenholme, 1998; Gulliver *et al*., 2001; Muir *et al*., 2015; Tierney *et al*., 2016) and several have identified uptake of Sellafield ^{14}C within the tissues of marine and intertidal organisms, leading to enrichment above ambient background (e.g. Begg *et al*., 1992; Cook *et al*., 1995, 1998, 2004), while others have established the role of molluscs in ^{14}C uptake and accumulation within the inter-tidal environment (Cook *et al*., 2004; Muir *et al*., 2015; Tierney *et al*., 2016). However, none have considered the marine ecosystem in detail. There has also been relatively little research on Sellafield ^{14}C beyond the Irish Sea. The net northerly movement of water through the North Channel dictates the long-term dilution and dispersion of Sellafield marine discharges (Dunster, 1998), with >99% of Sellafield ^{14}C dispersed through the North Channel (Gulliver *et al*., 2001). Using the highly soluble caesium isotopes, ^{134}Cs and ^{137}Cs, Jefferies *et al*., (1973) calculated transit times to the North Channel from Sellafield (then Windscale) in the region of 1.1 - 1.8 years. A shorter transit time was reported by Kershaw and Baxter (1995) of approximately 1 year, however a study on Sellafield releases of ^{99}Tc observed a further reduced transit time of 3 months (Kershaw *et al*., 2004). These studies show that Irish Sea circulation is highly variable and it is difficult to estimate a transit time to the North Channel and beyond, for Sellafield releases. Transit times for ^{14}C within the DIC fraction of seawater would, nevertheless, be similar to these relatively conservative radionuclides and, over a period of 3 months to a year, sufficient mixing should occur within the Irish Sea for a relatively homogenous activity (on short time scales) to reach the North Channel. From the North Channel, dissolved ^{14}C is carried around the Scottish coastline by the Scottish Coastal Current (McKay *et al*., 1986; Hill and Simpson, 1988) and the Fair Isle Current (Turrell and Henderson, 1990) into the North Sea (Gulliver *et al*., 2004).

Enriched ^{14}C activities in the DIC fraction of seawater and within the tissue of several marine species have been observed along the Scottish coastline (Cook *et al*., 1998). Similarly, a recent study (Tierney *et al*., 2016) demonstrated that despite ^{14}C activities reducing with distance from Sellafield due to dilution, mollusc shells on the north-west Scottish coastline were enhanced above ambient background.

This research forms the second half of a two-part study examining the uptake and transfer of Sellafield-derived ^{14}C within the Irish Sea and West of Scotland (WoS) marine ecosystems. In this study, the West of Scotland (Figure 4.1) is designated as *far-field*,

relative to Sellafield ^{14}C inputs. The *near-field* encompasses the Irish Sea, and is examined in Part 1 (Muir *et al*., 2017). Previous studies (Cook *et al*., 1998; Tierney *et al*., 2016) have observed Sellafield-derived ^{14}C enhancements in selected offshore and intertidal species in the WoS, therefore it is important to consider ^{14}C uptake within the wider WoS marine ecosystem. The overarching objectives are detailed in Part 1 (Muir *et al*., 2017). This study (Part 2. The West of Scotland) investigates, in detail, ^{14}C activities within the biotic and abiotic components of the WoS marine ecosystem, including that of commercially important fish/crustacean species and the transfer of ^{14}C through the marine food web. Due to its continuing discharge from Sellafield, long half-life and high bioavailability, it is important to gain an understanding of the transport, uptake and ultimate fate of ^{14}C within these marine ecosystems, not only with regard to past, current and future authorised ^{14}C discharges, but also in the unlikely event of a nuclear accident.

4.1.2 Study Areas

Samples were predominantly collected from 3 areas in the WoS; the North Channel, the Clyde Sea and the Firth of Lorn.

4.1.2.1 North Channel

The North Channel connects the northern end of the Irish Sea with the north-east Atlantic Ocean via the Clyde Sea. The channel narrows to 30 km in width and the seabed is characterised by rocky outcrops and localised enclosed deeps such as Beaufort's Dyke (Wilding *et al*., 2005a). Compared to the Irish Sea, the North Channel is relatively deep, averaging 90 m, and the dyke descends to 312 m (Callaway *et al*., 2011). Flow rates within the Irish Sea are typically low; however, the geomorphology of the North Channel means that the tidal flow here can be relatively fast at up to 1.5 m s^{-1}. A net northerly flow though the North Channel exists (Ramster and Hill 1969, Howarth 1982, Gulliver *et al*., 2001), but flow direction is seasonally variable and can be reversed (Dabrowski *et al*., 2010). Due to high flow rates, the central channel substrate is mainly rock and gravel with finer material deposited to the east, proximate to the Great Plateau (Wilding *et al*., 2005a). Beaufort's Dyke was used as a munitions disposal ground by the UK military from end of World War I until 1972 (Fisheries Research Services, 1996) and, perhaps as a consequence, there is a lack of studies on the benthic ecosystem within the North Channel.

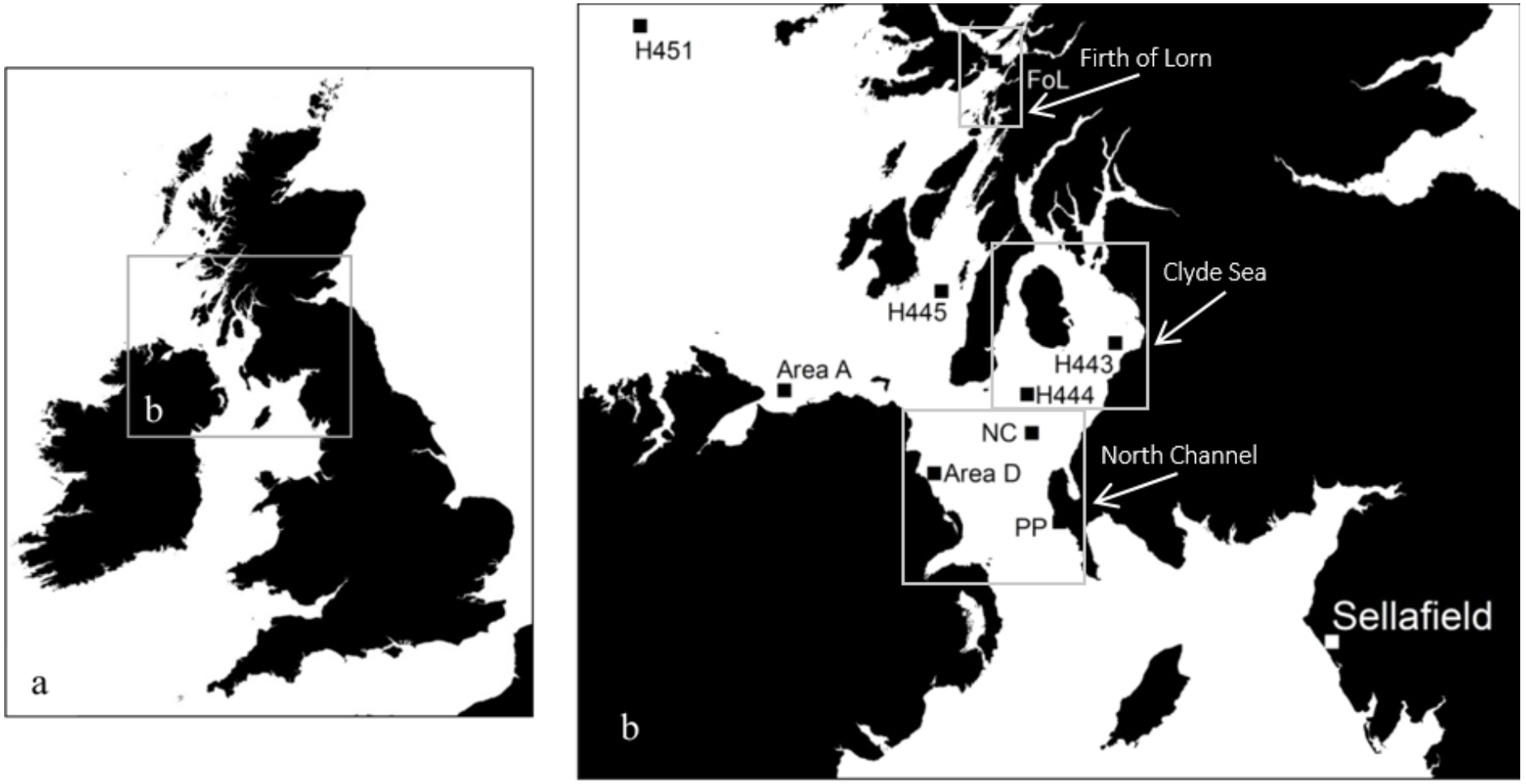

Figure 4.1. Map of the British Isles and Ireland (a) with inset (b) showing West of Scotland study sites.

4.1.2.2 Clyde Sea

The Arran Basin is the predominant depositional basin within the Clyde Sea, where deep water can become isolated in summer and renewed during winter when currents carrying dense water flow over the Great Plateau (Wilding *et al*., 2005b). Sills at the entrances of sea lochs north of the Arran Basin produce a similar effect where loch bottom waters can also become isolated (Edwards and Sharples, 1986). As the water is only exchanged intermittently, the deep benthic environment of the Clyde Sea is particularly vulnerable to anthropogenic impacts (Wilding *et al*., 2005b). The subtidal environment mainly consists of fine grained layered muds which extend from the Arran Basin into the basins of the sea lochs (Moore 1931, Wilding *et al*., 2005b). Benthic communities are characterised by high abundances of heart urchin (*Echinocardium cordatum* and *Brissopsis lyrifera*) and brittle stars (*Amphiura spp*), while bivalves, polychaetes and the burrowing decapod, *Nephrops norvegicus* (henceforth referred to as *Nephrops*), are also present (Pearson *et al*., 1986). Fishing pressure has reduced the volume of fish caught in the Clyde Sea significantly (Thurstan and Roberts, 2010). Historically, the area contained important fisheries for herring (*Clupea harengus*), cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus*), saithe (*Pollachius virens*) and hake (*Merluccius merluccius*) but fishing yields have since collapsed (Thurstan and Roberts, 2010, Heath and Speirs, 2012). Currently, the important remaining fisheries in the Clyde Sea are for *Nephrops* and scallops (*Pecten maximus* and *Chlamys opercularis*) (Thurstan and Roberts, 2010).

4.1.2.3 Firth of Lorn

The Firth of Lorn is located on the west coast of Scotland to the east and south east of the Isle of Mull. The Corryvreckan whirlpool lies to the south of the Firth of Lorn where a strong tidal race produces flow speeds up to 4.5 m s^{-1} which has a significant impact on local sediment transport (Howe *et al*., 2015). The central firth area contains depositional basins at 150 m depth and thick sequences of muds are also found in the many sea lochs that surround the firth (Howe *et al*., 2015). Sediments within the deep basins support dense fields of crinoids (*Leptometra celtica*) and large numbers of northern sea-fans (*Swiftia pallida*) are found on sediment-covered stony sea-beds (Davies, 1999). The diversity of habitats here is reflected in the existence of a number of nationally-rare benthic species (Plaza and Sanderson, 1997). Due to its biological

richness, the Firth of Lorn is designated as a Special Area of Conservation (SAC). This has resulted in a ban on scallop dredging in the area, previously an important fishery. *Nephrops*, found in the muddy habitats, is now the single most significant fishery. Although not a major spawning ground, the Firth of Lorn has been identified as an important nursery ground for larval and juvenile fish from a wide range of species (Fox and Lappalainen, 2014).

4.2 Methodology

Sampling and analytical techniques utilised are described in detail in Muir *et al*. (2017) and summarised here in relation to the sites sampled which are shown in Figure 4.1 and detailed in Table 4.1. Seawater, sediment and benthic organisms were collected in the Firth of Lorn (station FoL) in April 2014, on-board the RV Calanus. Plankton samples were collected at the same site in August 2014, together with additional seawater samples. A sampling campaign within the Irish Sea was conducted in June 2014 on-board the RV Prince Madog, and included the North Channel (station NC) where the same suite of sampling techniques was used. Additional North Channel seawater samples were collected from the coastline near to Portpatrick (station PP) in April 2014 and August 2014. A number of fish and crab samples were collected by the Marine Scotland Science's West of Scotland demersal fish survey, from the RV Scotia during November 2014. These samples were predominantly taken from the Clyde Sea (H443 and H444), however, some were also collected further north, between the Isles of Gigha and Islay (H445) and off the west coast of Tiree (H451). The Agri-Food and Biosciences Institute, Northern Ireland (AFBI-NI) collected shellfish samples from off the northern Irish coastline (Areas A and D) in February 2015.

Table 4.1. Sampling station details for the West of Scotland

Sampling station	Study area	Date sampled	Station co-ordinates	Sample type(s)
FoL	Firth of Lorn	April 2014; August 2014	56 23.83 N, 05 36.86 W	seawater, sediment, plankton, benthic organisms
NC	North Channel	June 2014	55 08.85 N, 05 18.93 W	seawater, sediment, plankton, benthic organisms
PP	North Channel	April 2014; August 2014	54 50.33 N, 05 06.98 W	seawater
H443	Clyde Sea	November 2014	55 27.79 N, 04 48.95 W	fish survey
H444	Clyde Sea	November 2014	55 16.58 N, 05 20.39 W	fish survey
H445	Sound of Jura	November 2014	55 37.72 N, 05 53.54 W	fish survey
H451	Outer Hebrides	November 2014	56 27.81 N, 07 50.16 W	fish survey
Area A	North Channel (north-west)	February 2015	55 14.28 N, 06 49.28 W	scallop survey
Area D	North Channel	February 2015	54 58.20 N, 05 54.32 W	scallop survey

4.2.1 Seawater ^{14}C biogeochemical fractions

Surface water was collected to measure ^{14}C activity in the four biogeochemical fractions; dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate inorganic carbon (PIC) and particulate organic carbon (POC). Surface samples from 2 m depth were collected on research vessels at stations NC and FoL by pumping 160 l of seawater on board. Additional 160 l samples were collected, at high tide using 20 l carboys, from the North Channel coastline at Port Patrick. The water was filtered through 0.7 μm glass fibre filters with particulate material used for analysis of PIC and POC. Several 500 ml aliquots of filtrate were collected in foil bags for analysis of DIC. Further aliquots of 500 ml were collected in glass bottles for analysis of DOC with 1 ml of (85%) orthophosphoric acid added to liberate DIC and fix the organic carbon content.

4.2.2 Sediment organic content

Sediment cores were retrieved from stations NC and FoL using an OSIL maxi-corer. Cores were approximately 30 cm in depth and sectioned into 1 cm vertical increments

which were initially frozen for storage. The sections were later thawed, oven dried at 40°C and ground into a fine powder. The ^{14}C activity in the organic component of sediment was measured within four depth increments (0-1 cm, 5-6 cm, 10-11 cm and the base of the core) in one core from each site.

4.2.3 Biota

Beam trawls and Van Veen grabs were utilised to sample the benthic biota at NC and FoL. A range of organisms was collected and identified, where possible, to species level. Fish and shellfish stock surveys (by AFBI and Marine Scotland Science) using bottom trawls provided additional fish and crab samples. Muscle/soft tissue was subsampled and freeze dried. Where more than one individual of a species was collected, samples were proportionally combined and multiple samples were made if six or more individuals were available. Similarly, where several relatively analogous species had been collected with few individuals of a specific species, the samples were combined (e.g. starfish). Plankton nets were utilised at NC and FoL to collect phytoplankton (80 – 270 μm mesh size) and zooplankton (> 270 μm). Whole plankton samples were freeze dried.

4.2.4 ^{14}C analysis procedure

To measure the ^{14}C activity, organic samples (DOC, POC, organic sediment, biota) were combusted in sealed quartz tubes according to the method of Vandeputte *et al*. (1996) and inorganic samples (DIC, PIC) hydrolysed with HCl (1 M) to liberate CO_2. The gas was cryogenically trapped and purified and graphite was produced from 3 ml subsamples according to the method of Slota *et al*. (1987). Sample $^{14}C/^{13}C$ isotope ratios were measured on the SUERC 250 KV SSAMS or the 5 MV tandem AMS (Freeman *et al*., 2008, 2010) and with quality assurance standards described in Naysmith *et al*. (2011) and Dunbar *et al*. (2016). Stable isotope ($\delta^{13}C$) ratios were measured offline on a VG SIRA 11 isotope ratio mass spectrometer for calibration of natural fractionation of the measured ^{14}C. ^{14}C results were calculated relative to the international standard (oxalic acid II, SRM-4990C) as ^{14}C activity ratios (fraction modern, $F^{14}C$). Fraction modern results were converted to specific activities (Bq kg^{-1} C) using the regime for calculating enhanced activity samples described by Mook and van der Plicht (1999). Uncertainties are typically less than 0.5% of the measured activity.

4.3 Results and Discussion

4.3.1 North Channel

4.3.1.1 Seawater ^{14}C Biogeochemical Fractions

The ^{14}C values for the biogeochemical fractions of the surface seawater samples from stations PP and NC are presented in Table 4.2. The DIC component was enriched in ^{14}C at both sites and at all 3 sampling dates, in line with the dissolved inorganic form of ^{14}C discharged from Sellafield. The POC fraction was also enriched at station NC but marginally depleted at station PP for both the April and August sampling periods. The $\delta^{13}C$ values of the POC fractions at station PP were lower than that at the NC station, which indicates that a greater proportion of the material at station PP was probably terrestrial in origin. This would explain the reduced activities as terrestrially-derived run-off could potentially contain a significant proportion of "old carbon", resulting in a dilution effect. Surface water collected during June 2014 from station NC was also enriched in ^{14}C within the PIC fraction. This enrichment in the PIC could result from movement of fine, ^{14}C enriched material from the intertidal zone as described by Tierney *et al*. (2016). The PIC fraction was significantly depleted at station PP and the lower $\delta^{13}C$ values for these samples indicate that a greater proportion of the material was again terrestrial in origin. The single DOC sample containing enough dissolved carbon for ^{14}C analysis was significantly depleted and had a $\delta^{13}C$ value typical of terrestrial carbon, indicating significant run-off of "old carbon" from land. ^{14}C activities measured in the same fractions of seawater from the North Channel in 1989 (Cook *et al*., 1995) showed similar enrichment in the DIC fraction and depletion in the DOC and POC fractions, despite the increase in Sellafield ^{14}C marine discharges at this period. Also, at this time, North Channel PIC was depleted in comparison to the slight enrichment observed in 2014 at station NC; however, PIC was depleted in 2014 at station PP. The ^{14}C activity of the DIC at station PP was also measured in 1995 at the onset of increased Sellafield discharges (Cook *et al*., 1998) and was significantly enriched (430 ± 4 Bq kg^{-1} C) compared to the activities measured in this study. Sellafield discharges of ^{14}C were higher in the 12 months prior to sample collection in 1995 (8.7 TBq) relative to the 2014 sample collection (4.8 TBq). As the transit time of discharges from Sellafield to the North Channel is in the order of 3 months to >1 year (Jefferies *et al*., 1973; Kershaw and Baxter, 1995; Kershaw *et al*., 2004), the lower activities described here are most likely a direct result of the lower discharged activities in the preceding months.

Table 4.2. Gross and net specific ^{14}C activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ (‰ relative to VPDB) values from the four biogeochemical fractions of North Channel surface water samples from stations NC and PP. Net activities above the ambient background of 249 ± 1 Bq kg^{-1} C are in bold. Samples less than this are denoted as 'Depleted'.

Date Sampled (station)	**^{14}C specific activities (Bq kg^{-1} C ± 1σ) $\delta^{13}C$ (‰)**			
	DIC	PIC	DOC	POC
April 2014 (PP)	278 ± 2 **29 ± 2** (+1.1‰)	180 ± 1 **Depleted** (-2.0‰)	n/a	247 ± 1 **Depleted** (−22.1‰)
June 2014 (NC)	287 ± 1 **38 ± 2** (+3.9‰)	271 ± 1 **22 ± 1** (+1.1‰)	106 ± 1 **Depleted** (−26.8‰)	279 ± 1 **30 ± 1** (−19.4‰)
August 2014 (PP)	279 ± 1 **30 ± 1** (+7.5‰)	153 ± 1 **Depleted** (-0.8‰)	n/a	241 ± 1 **Depleted** (-22.0‰)

*n/a denotes insufficient carbon in sample for analysis

4.3.1.2 Sediment

The organic component at all depth increments of station NC sediment were depleted in ^{14}C (Table 4.3). The measured activities in the top 11 centimetres were relatively homogenous (204-210 Bq kg^{-1}) C, while the base activity (29-30 cm) was significantly depleted in comparison (135 Bq kg^{-1}). The large variety of benthic species found at this station, (discussed below) demonstrates that this is a highly biologically active site and the relatively homogeneous nature of the surface sediments is likely to be caused to a significant degree by intensive bioturbation. The ^{14}C activity observed in the surface sediment is depleted, which contrasts with the ^{14}C enrichment observed in surface water POC at station NC. POC may be rapidly scavenged from the water column and/or the surface sediment resulting in a very low flux and incorporation of Sellafield-derived ^{14}C into surface sediments. In addition, the build-up of higher activity material could also be masked through effective mixing to depth of ^{14}C-enriched organic material with significant quantities of old, ^{14}C-depleted organic material in the sediments, resulting in a dilution effect (see Muir *et al.*, 2017). Furthermore, physical transport of ^{14}C enhanced particulate material from this site by currents could also reduce the volume reaching the sediment and this has previously been suggested as an important mechanism for the transport of enhanced fine inorganic material in northern Irish Sea coastal sites (Tierney *et al.*, 2016).

Table 4.3. Sediment organic fraction gross ^{14}C activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ values (‰ relative to VPDB) in selected horizons for station NC. Values less than ambient background (249 ± 1 Bq kg^{-1} C) are denoted as 'Depleted'.

Horizon depth (cm)	**Gross ^{14}C activity (Bq kg^{-1} C)**	**$\delta^{13}C$ (‰)**
0-1 (surface)	204 ± 1 **Depleted**	−21.7
5-6	210 ± 1 **Depleted**	−21.8
10-11	210 ± 1 **Depleted**	−21.8
29-30 (base)	135 ± 1 **Depleted**	-21.9

4.3.1.3 Biota

The ^{14}C activities of sampled biota at station NC are presented in Figure 4.2. All species analysed were enriched relative to the ambient background and mostly varied between 280 and 330 Bq kg^{-1} C with whiting (*Merlangius merlangus*) having a significantly higher activity (413 ± 2 Bq kg^{-1} C). In contrast, phytoplankton (280 ± 2 Bq kg^{-1} C) and zooplankton (283 ± 2 Bq kg^{-1} C) had amongst the lowest ^{14}C activities. Dab (*Limanda limanda*) (samples 1 and 2) showed intra-species variation, where the difference between the two samples, each consisting of 3 individuals, was approximately 42 Bq kg^{-1} C. Similar intra-species differences have been observed for dab in the Irish Sea (Muir *et al*., 2017) while other multiple samples of the same species/species group showed little or no intra-species variation.

Phytoplankton species have a relatively fast carbon turnover rate and short lifespan, and will readily incorporate ^{14}C from DIC during photosynthesis. The ^{14}C activities in DIC, phytoplankton and POC were comparable at station NC illustrating direct uptake of ^{14}C from ambient waters and implying that the POC is predominantly derived *in situ* from phytoplankton. The zooplankton sample from station NC was observed to consist largely of copepods (probably *Calanus finmarchicus* and/or *Calanus helgolandicus* due to their predominance in this area) with some ctenophores and ichthyoplankton. Although some

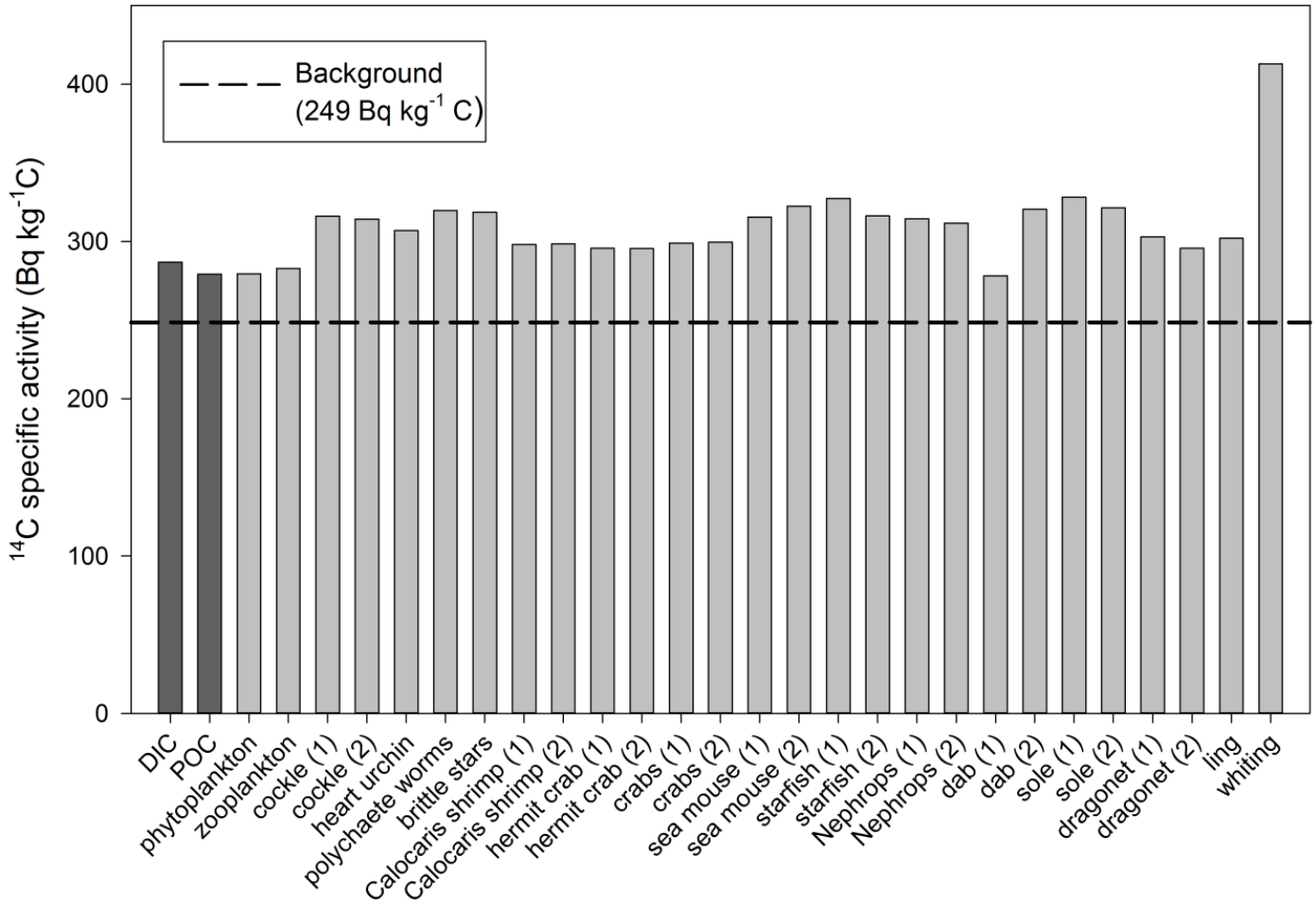

Figure 4.2. Gross specific ^{14}C activities (Bq kg^{-1} C) in benthic biota samples and seawater DIC and POC, collected at station NC. The dashed line indicates the measured background activity of 249 Bq kg-*1* C, measured in blue mussel (*Mytilus edulis*) shells obtained from the West Coast of Ireland.

zooplankton species are carnivorous, copepods feed directly on phytoplankton (Meyer-Harms *et al*., 1999). That zooplankton ^{14}C activity is also similar to that of phytoplankton, reflecting the ^{14}C activity of their primary source of food, and the transfer of ^{14}C through the food chain.

Although phytoplankton and zooplankton ^{14}C activities were amongst the lowest and the whiting activity was the highest, there is no obvious trend of increasing ^{14}C activity moving up the food chain. This corresponds to a general transfer of ^{14}C from primary producers to higher organisms with no concentration effect, as might be expected. Any variation in ^{14}C activity more likely derives from variations in the food source and the integration period of carbon uptake. Filter feeders, such as the common cockle (*Cerastoderma edule*) will incorporate ^{14}C from the plankton and POC that they ingest (Iglesias *et al*., 1992). Organisms like polychaete worms, heart urchin (*Echinocardium cordatum*), brittle stars, Calocaris shrimp (*Calocaris macandreae*) and the hermit crab (*Pagurus bernhardus*) are predominantly detritivorous, feeding on the organic material falling from the water column. The relative ^{14}C enhancement above background in these species, confirms the supply of ^{14}C enriched organic material to the sediment surface. Other crab species (*Goneplax rhomboides, Atelecyclus rotundatus, Inachus sp.*) will predate on smaller organisms as well as feeding on detritus. The sea mouse (*Aphrodita aculeata*), *Nephrops*, starfish (*Asterias rubens*, *Crossaster papposus*, *Luidia sarsii,* Asteroidea *sp.*) and fish species (dab, sole, dragonet (*Callionymus lyra*), ling (*Molva molva*), whiting) are predatory, feeding on other benthic organisms. These species have higher ^{14}C activities than the plankton groups indicating that organisms occupying higher trophic levels are integrating ^{14}C over a longer period of time, including periods of higher ambient activities. For example, many of the analysed benthic species are only locally mobile (e.g., brittle star, sea mouse and starfish). Therefore, their high activities relative to that of phytoplankton are a result of uptake during a period of higher ambient activity, corresponding to transient ^{14}C enrichment in the DIC fraction of seawater, which was subsequently passed through the food chain. Due to their relatively longer life-span, an integrated higher activity in these species is now observed. Conversely, whiting are highly mobile and the comparatively high ^{14}C activity in this sample probably results from sampling individuals which had previously foraged in the Irish Sea. Demersal fish within the Irish Sea have ^{14}C activities greater than 400 Bq kg^{-1} C, as do their prey items (Muir *et al*., 2017). Therefore, it is likely that station NC whiting had migrated from the more ^{14}C-enriched Irish Sea.

4.3.2 ^{14}C activities in Fish and Shellfish Survey species

Scallops are filter feeders and are, therefore, likely to have a similar ^{14}C activity to phytoplankton and to ambient DIC. The ^{14}C activity of scallops (Figure 4.3) collected at Area A (249 ± 1 Bq kg^{-1} C) was identical to background, whereas scallops from Area D were enriched (283 ± 2 Bq kg^{-1} C). Area A is located on the northern coast of Northern Ireland where the influence of Atlantic Ocean water should be greater and this is demonstrated in the observed ^{14}C activity being equal to background. Area D, in the North Channel, is affected by a southerly current which carries Atlantic water down the western edge of the North Channel (Bowden 1980; Dabrowski *et al*., 2010). Despite there being some Atlantic influence, the effect of Sellafield ^{14}C discharges is still observable in this sample.

The ^{14}C activities of fish and crab samples from the Marine Scotland Science surveys are also shown in Figure 4.3. Samples from the Clyde Sea area (H443 and H444) were ^{14}C enriched, although fish samples typically had a lower activity here than fish at station NC. Haddock (*Melanogrammus aeglefinus*), primarily a benthic feeder, and herring (*Clupea harengus*), a planktivore, had relatively similar activities at station H443 (296 ± 2 Bq kg^{-1} C and 283 ± 2 Bq kg^{-1} C respectively) indicating little variation in ^{14}C activity in the water column. In comparison to station NC, whiting at H443 had a significantly lower activity (288 ± 2 Bq kg^{-1} C), again indicating that station NC whiting had spent time foraging in an enriched area, probably within the Irish Sea. Haddock samples collected further north and west (station H445) were also enriched (286 ± 2 Bq kg^{-1} C) but had a reduced activity relative to Clyde Sea haddock. Edible crab (*Cancer pagurus*) activity showed little variation between stations H443 (292 ± 2 Bq kg^{-1} C), H444 (304 ± 2 Bq kg^{-1} C) and H445 (288 ± 2 Bq kg^{-1} C). The activities at these stations are similar to those measured in other crustaceans at station NC, suggesting there was little difference in benthic ^{14}C activity between the North Channel and Clyde Sea.

Station H451 (situated approximately 74 km to the west of the Outer Hebrides) was the most remote sampling area from Sellafield in this study. Only monkfish *(Lophius piscatorius*) were sampled from this station and the measured ^{14}C activity (250 ± 1 Bq kg^{-1} C) is indistinguishable from ^{14}C background and reflects the influence of Atlantic waters. Irish Sea residual waters (with enriched ^{14}C activity) are carried northwards by currents which closely hug the Scottish coastline (McKay *et al*., 1986; Hill and Simpson, 1988).

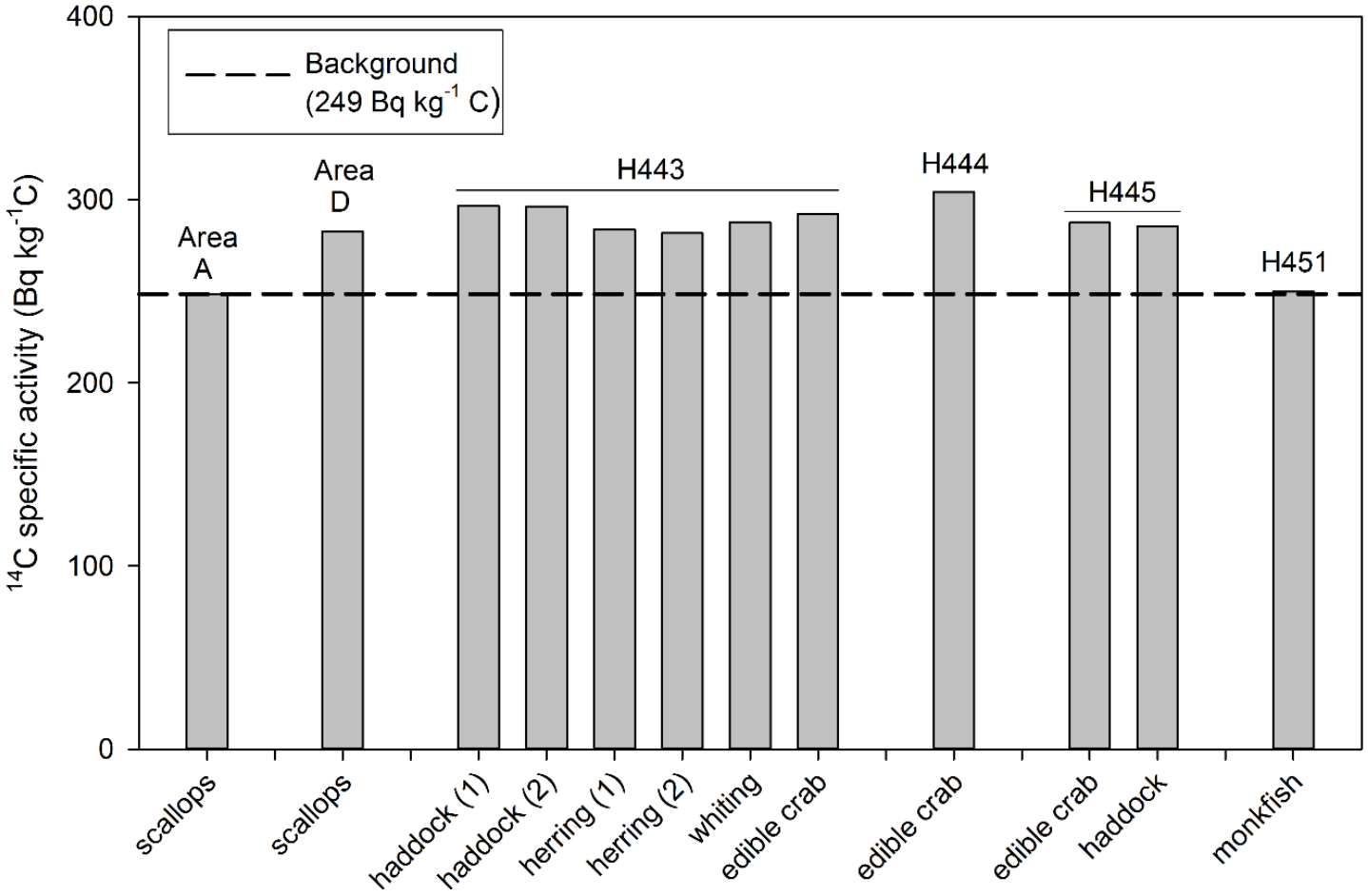

Figure 4.3. Gross specific ^{14}C activities (Bq kg^{-1} C) in species collected in the Clyde Sea and other areas during fisheries surveys. The dashed line indicates the measured background activity of 249 Bq kg^{-1} C, measured in blue mussel shells obtained from the West Coast of Ireland.

This result signifies that Sellafield ^{14}C has little influence in offshore waters dominated by Atlantic water to the west of the Scottish Coastal Current, at least in the benthic environment that monkfish inhabit, and at the time of sampling.

4.3.3 Firth of Lorn

4.3.3.1 Seawater ^{14}C Biogeochemical Fractions

Surface water sample activities (Table 4.4) showed an enriched DIC ^{14}C activity at station FoL during the period when benthic biota were sampled in April 2014 and when plankton were sampled in August 2014. In contrast, PIC and POC activities were depleted at both sampling periods. The reduction in DIC activity between April and August demonstrates that the ambient ^{14}C activity is changeable over short periods of time despite being distant from the discharge source. This could be due to the variation in discharged activity but local current direction influencing the sources of local water will also have an impact on ambient activities. However, station FoL DIC activities are similar to those observed at stations NC and PP. This suggests that at the time of sampling, there was relatively little dilution of DIC ^{14}C between these two sites after mixing between Atlantic and Irish Sea water in the North Channel, and that there was little further input of Atlantic water to this water mass. DIC sampled at a coastal site further north in Scotland in 1995 (Cook *et al*., 1998) showed a comparable ^{14}C activity (272 ± 4 Bq kg^{-1} C), despite higher discharges in the year preceding sampling. The observed activity could arise from further dilution of residual Irish Sea water with Atlantic water. Although the small dataset from both these studies makes it difficult to draw any firm conclusions on hydrodynamics, it does highlight a general reduction in ^{14}C activity with distance from Sellafield and the possibility of using Sellafield-derived ^{14}C as a tracer for water masses in the north of Scotland.

In the case of the PIC, carbon derived from terrestrial sources could affect the activity although the $\delta^{13}C$ indicates that the material is predominantly of marine origin. This would imply a dilution by PIC of pre-Sellafield origin as described for the intertidal environment in Tierney *et al*. (2016). In the case of the POC, the April 2014 sample is much more depleted than the August 2014 sample. The April sample has a $\delta^{13}C$ value that is 3.1‰ lower than the August sample and would therefore imply a greater effect from carbon derived from the terrestrial environment in early spring. Also, the increase in POC activity between April and August probably results from increased primary production over the

spring and summer months, converting more ^{14}C enriched DIC into phytoplankton with subsequent transfer through the food chain resulting in a higher POC activity.

Table 4.4. Gross and net specific ^{14}C activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ (‰ relative to VPDB) values from the four ^{14}C biogeochemical fractions of station FoL surface water samples. Net activities above the ambient background of 249 ± 1 Bq kg^{-1} C are in bold. Samples with values lower than this are marked as 'Depleted'.

Date	**^{14}C Specific Activities (Bq kg^{-1} C ± 1σ) $\delta^{13}C$ (‰)**			
	DIC	PIC	DOC	POC
April 2014	298 ± 2 **49 ± 2** (0‰)	183 ± 1 **Depleted** (-2.7‰)	n/a	198 ± 1 **Depleted** (−24.5‰)
August 2014	277 ± 1 **28 ± 1** (+7.7‰)	196 ± 1 **Depleted** (-3.4‰)	n/a	234 ± 1 **Depleted** (−21.4‰)

*n/a denotes insufficient carbon in sample for analysis

4.3.3.2 Sediment

Organic sediment ^{14}C activities at station FoL are all below the ambient background (Table 4.5). They are again uniform throughout the top 11 cm (208-209 Bq kg^{-1} C) with a small decrease in activity at the core base, and very similar to station NC for the top 11 cm (204-210 Bq kg^{-1} C) (Table 4). Again, sediment homogeneity is consistent with intensive bioturbation as a result of the high biological activity at this site. Surface sediment ^{14}C activity falls between the depleted activities measured in surface water POC in April and August 2014 indicating that this POC material is deposited in the sediment.

Table 4.5. Sediment organic fraction gross and net ^{14}C activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ values (‰ relative to VPDB) in selected horizons for station FoL. Values less than ambient background (249 ± 1 Bq kg^{-1} C) are denoted as 'Depleted'

Horizon depth (cm)	**Gross ^{14}C activity (Bq kg^{-1} C)**	**$\delta^{13}C$ (‰)**
0-1 (surface)	208 ± 1 **Depleted**	−22.0
5-6	208 ± 1 **Depleted**	−21.9
10-11	209 ± 1 **Depleted**	−21.8
33-34 (base)	200 ± 1 **Depleted**	-21.6

4.3.3.3 Biota

Phytoplankton at station FoL were slightly depleted below background (241 ± 1 Bq kg^{-1} C) and zooplankton were significantly depleted (227 ± 1 Bq kg^{-1} C). All other samples were enhanced and relatively uniform in activity (Figure 4.4). The reduced phytoplankton ^{14}C activity at FoL questions the previously stated convention that phytoplankton activity would be expected to reflect DIC activity as is observed at station NC. This could be explained by the phytoplankton sample containing some POC with a depleted ^{14}C activity. However, the zooplankton ^{14}C activity, which is significantly depleted relative to that of phytoplankton, suggests that there may be a more complex explanation as this sample, like its equivalent at station NC, was comprised almost totally of copepods which feed directly on phytoplankton. This aspect of the study will require further sampling and analysis in the future as the value of 227 Bq kg^{-1} C is difficult to reconcile with general ocean ambient background activities, although upwelling of older deep water could provide a source for below background ^{14}C activities.

As benthic organisms were enriched in ^{14}C in April 2014, it follows that their food source must have also been enriched. Phytoplankton, at the base of the food chain, and zooplankton (dominated by copepods), as grazers of phytoplankton, were therefore likely

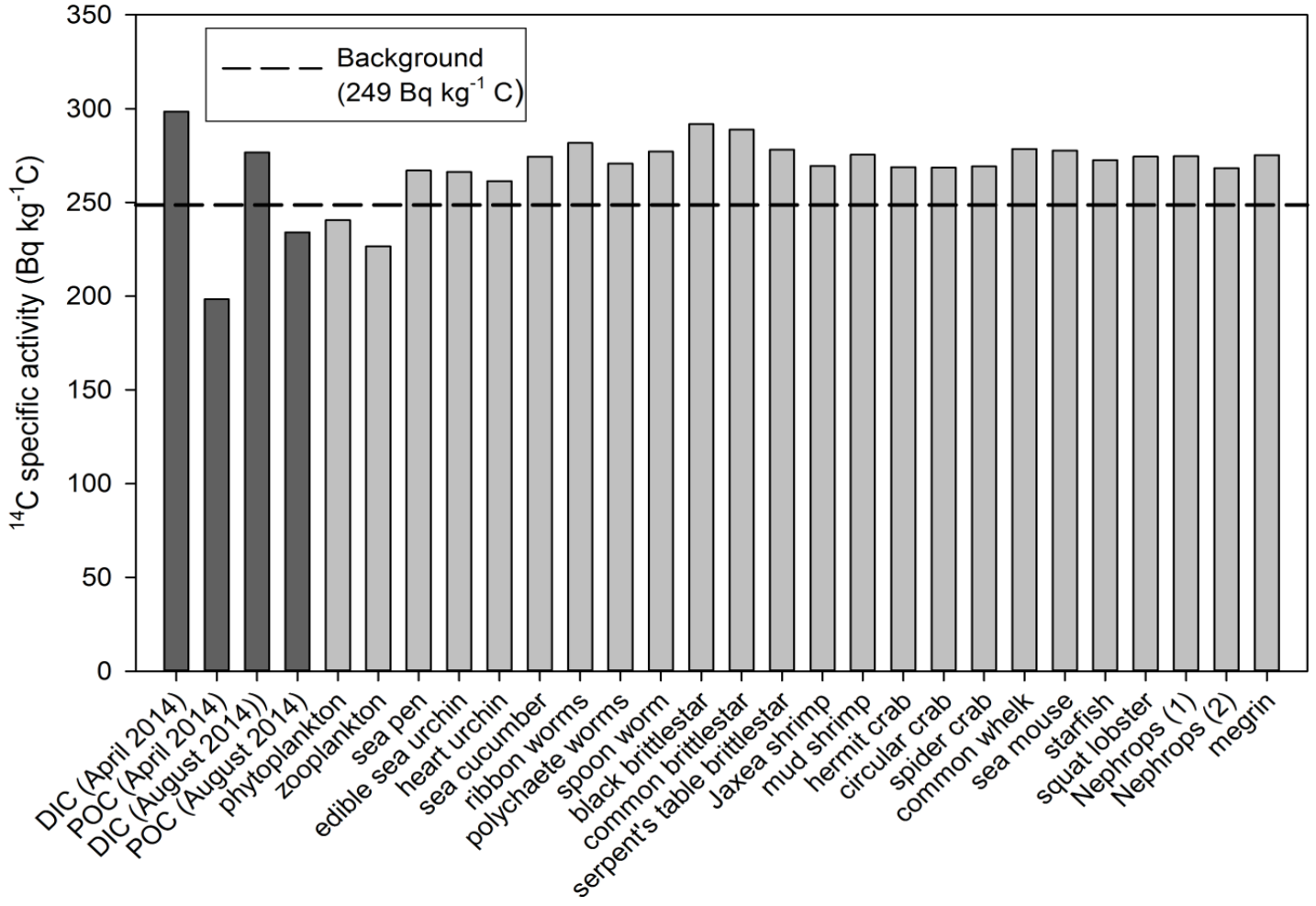

Figure 4.4. Gross specific ^{14}C activities (Bq kg^{-1} C) in benthic biota samples and seawater DIC and POC, collected at station FoL. The dashed line indicates the measured background activity of 249 Bq kg^{-1} C, measured in blue mussel shells obtained from the West Coast of Ireland.

to be enriched in ^{14}C prior to when plankton were sampled and ^{14}C subsequently transferred along the food chain to other organisms. It is possible that plankton and water samples were taken shortly after a change in water mass. If, after a period of stronger Atlantic influence, the water mass became increasingly dominated by Irish Sea residual water, an increase in DIC ^{14}C activity from background or potentially from below background (depending on the age and ^{14}C activity of the Atlantic water) to above background would follow. Although this would result in an increase in plankton activity, this would take time to develop, and therefore result in the ^{14}C enrichment observed in the DIC fraction and depletion in plankton activities at the time of sampling. The fact that other organisms were all enriched in ^{14}C indicates that, in the long-term, the Firth of Lorn is dominantly supplied by residual Irish Sea water, resulting in these longer-lived organisms integrating ^{14}C over relatively long periods.

A wide range of benthic organisms were collected at station FoL and results are presented in Figure 4.4. The sea pen (*Funiculina quadrangularis*) is a colonial planktivorous, passive suspension feeder and its ^{14}C enrichment (267 ± 2 Bq kg^{-1} C) confirms that primary producers in this area were enriched in ^{14}C in the period prior to sampling. The edible sea urchin (*Echinus esculentus*) is an omnivore and could integrate ^{14}C from grazing on algae or predating upon other invertebrates. A number of species which are predominantly detrivorous were sampled, including the heart urchin, sea cucumber (Holothuroidea sp.), ribbon worm (Nemertea sp.), polychaete worms, spoon worm (*Maxmuelleria lankesteri*), brittle star species (*Ophiocomina nigra*, *Ophiothrix fragilis* and *Ophiura albida*), burrowing shrimp species (*Jaxea nocturna*, *Callianassa subterranea*), and crab species (*Pagurus prideaux, Atelecyclus rotundatus, Inachus* sp.). The enriched ^{14}C activities measured in these organisms proves that ^{14}C enhanced organic material is supplied to the sediment surface and is being scavenged by the large number of detrivores inhabiting this area. The overall extent of Sellafield ^{14}C ecosystem uptake and biological transfer is shown by the enriched activities found in predatory organisms from station FoL, including the common whelk (*Buccinum undatum*), sea mouse, starfish species (*Asterias rubens*, *Crossaster papposus, Luidia sarsii*), squat lobster (*Munida rugose*), *Nehrops* and megrin (*Lepidorhombus whiffiagonis*).

Small reductions in ^{14}C activities of biota are observed at station FoL compared to those of station NC, with an average reduction in the enhancement over ambient background of 13%. This confirms that Irish Sea residual water is the dominant source of water to station

FoL and so we might expect to see similar enhancements in biota beyond station FoL until significant dilution of the Scottish Coastal Current occurs. Clyde Sea samples were similar to station NC but fish ^{14}C activities were generally lower. At each site, the activities of organisms are relatively homogenous, despite the large variation in species. The range in species covers significantly different lifespans, different metabolic rates and different feeding behaviours and suggests that the overall Sellafield effect at these sites, particularly at station FoL, is relatively constant. Variable mixing patterns of seawater in the West of Scotland with residual Irish Sea waters, at any given time, may cause small changes in the overall ^{14}C DIC activity. However, any short-term variations in ambient DIC ^{14}C activity are likely to be minor in comparison to sites closer to Sellafield, particularly in the north-east Irish Sea which presents greater heterogeneity.

4.3.4 Comparison of far-field (West of Scotland) and near-field (Irish Sea) results

Comparing the results presented here with data from the Irish Sea (Muir *et al*., 2017) allows us to better understand the scope of transport of ^{14}C to the WoS and ecosystem uptake in this region. A general reduction in DIC ^{14}C activity with increasing distance from Sellafield is observed when comparing measurements from the north-east Irish Sea (546 ± 2 Bq kg^{-1} C) to WoS results. The relative decrease in western Irish Sea DIC activity (264 ± 1 Bq kg^{-1} C), compared to WoS sites, supports previous work which showed that >99% of discharged ^{14}C leaves the Irish Sea through the North Channel (Gulliver *et al*., 2001). Organic sediment activities at stations NC and FoL are depleted, whereas enriched activities are observed in the north-east Irish Sea (e.g. 298 ± 1 Bq kg^{-1} C in surface sediment). This shows the greater flux of enriched material to the sediment in the north-east Irish Sea as would be expected at a site much closer to the ^{14}C source.

In comparison with organisms obtained from the north-east Irish Sea (station EB), it is apparent that ^{14}C activities in West of Scotland organisms are significantly reduced (Figure 4.5). Although high ^{14}C activities have been observed in some western Irish Sea (station WB) organisms, most results at station WB are comparable to, or below the activities observed for the North Channel, Clyde Sea and Firth of Lorn stations. The high activity of whiting collected at station NC is clearly identified as an outlier, however, the median activity in benthic biota from station WB is actually less than the equivalent at station NC. This indicates that the northern extremity of the North Channel is receiving similar or higher ^{14}C-enriched DIC inputs than the western Irish Sea, as confirmed by the DIC data.

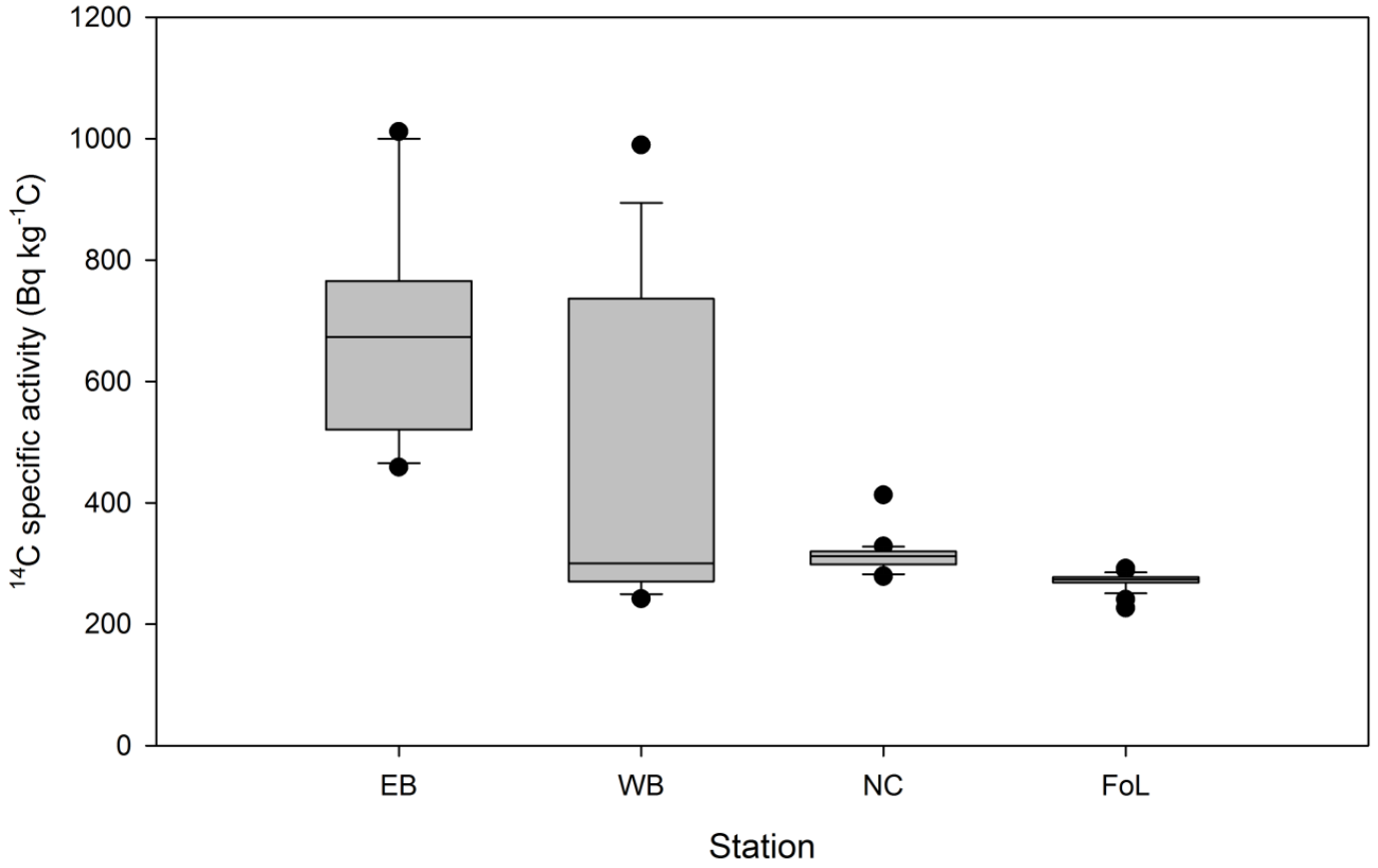

Figure 4.5. Boxplot of ^{14}C activities (Bq kg^{-1} C) from all biota samples measured in Irish Sea stations EB and WB (from Muir *et al*., 2017) and West of Scotland stations NC and FoL. Boxes describe respective the interquartile range and whiskers describe the 5th and 95th percentiles. The solid black line within boxes indicates respective median values. Each black dot represents a singular outlier with respect to the majority of the data for that site.

Results from the Irish Sea show a much wider range of activities to that of the West of Scotland. It is likely this is due to monthly changes in ^{14}C discharges from Sellafield having a greater impact on the Irish Sea ambient ^{14}C activity, ultimately increasing the variability. Transfer and mixing processes within the Irish Sea result in a more homogenous activity being transferred through the North Channel and northwards along the West of Scotland where mixing with Atlantic water can reduce the ambient activity with distance from Sellafield (Cook *et al*., 1998; Gulliver *et al*., 2001; Tierney *et al*., 2016).

Relatively low ^{14}C activities measured in plankton groups both in the Irish Sea and West of Scotland are identified as being statistical outliers and are depicted in Figure 4.5 as black dots below the interquartile range. In the Irish Sea, this most likely occurs as a consequence of the very low Sellafield ^{14}C discharge during the sampling period (Muir *et al*., 2017). In recent years, it appears that highest monthly discharges of ^{14}C coincide with autumn-winter months (Muir *et al*., 2017). Discharges coinciding with plankton blooms during the spring and summer could result in higher organic activities and increased ^{14}C transfer through the food chain (Cook *et al*., 1995). It is not clear if the recent discharge policy has followed this protocol or is coincidental, as previously there were no trends in discharge activity. Discharging more ^{14}C in periods of low primary production will probably result in a net reduction in the overall ecosystem ^{14}C uptake within the north-east Irish Sea. Due to intensive mixing within the Irish Sea, and the time taken for ^{14}C to be transported northwards, it is unlikely this would have a similar impact beyond the North Channel. However, it is conceivable that due to reduced uptake within the Irish Sea, higher activity water will be transported north, potentially resulting in increased activities in West of Scotland biota, although this effect remains unconfirmed.

Radiation dose rates have been calculated for the Sellafield critical consumer group for ^{14}C activities measured in the north-east Irish Sea (Muir *et al*., 2017). These dose rates are negligible for ^{14}C activities which are significantly higher in comparison to the ^{14}C activities observed in commercially important species from the WoS sites. Assuming a WoS critical consumer group has the same consumption rates as the Sellafield critical consumer group (Garrod *et al*., 2015) and by using the highest activities measured in the WoS for fish (whiting 413 ± 2 Bq kg^{-1} C) and *Nephrops* (315 ± 2 Bq kg^{-1} C), the maximum dose received would be 0.59 μSv. This dose is 71% less than the maximum dose measured for the Sellafield critical consumer group (2.05 μSv) from ^{14}C discharges (Muir *et al*., 2017) and does not pose any radiological risk to the public.

4.4 Conclusions

Sellafield-derived ^{14}C is transported to the north-west of Scotland in the form of DIC. ^{14}C is highly bioavailable as demonstrated from the widespread ^{14}C enrichments observed in marine organisms. Although sediment activities are depleted in ^{14}C relative to ambient background, there is a clear pathway of uptake of ^{14}C by phytoplankton during photosynthesis, followed by transfer to planktivorous organisms and deposition of enriched particulate material. This organic material is rapidly consumed by detritus feeders and subsequently, ^{14}C is transferred through the entire benthic food web. It is apparent that sedimentation processes must be examined in more detail to determine the fate of ^{14}C at the sediment-water interface. Any future work should focus on the different organic carbon fractions within the sediment to better understand both the pathways for ^{14}C re-entry into the marine food and deposition of ^{14}C.

The extent of ^{14}C transport and ecosystem uptake is revealed by enriched activities at the Firth of Lorn (approximately 260 km from Sellafield). Although any increase in Atlantic water influence in the Firth of Lorn will reduce ambient ^{14}C activity, as shown by plankton activities, this area is dominated by inputs from a residual water component from the Irish Sea. However, the overall effect of dilution with Atlantic water is clear and ^{14}C activities reduce with distance from Sellafield, though a similar order of magnitude of ^{14}C enrichments in biota can be expected until there is significant dilution of the Scottish Coastal Current. The small dataset of surface water ^{14}C activities presented in this study shows the potential use of ^{14}C as a tracer for Irish Sea water and mixing processes in the UK marine environment.

Many of the organisms measured are commercially important species and the findings in this study suggest that ^{14}C enrichment is likely to be found in other unmeasured species from the same areas. It must be re-stated that the potential ^{14}C dose received from consumption of seafood in the WoS is negligible, and does not pose any radiological risk to consumers or local populations in the west of Scotland. However, due to its long half-life, high bioavailability and continued release, continued assessment of the fate of ^{14}C in the environment is important. To this purpose, ongoing work is utilising the data collected across this study to develop a predictive ecosystem model tracing the biological fate of ^{14}C released into the marine environment which, unlike other discharged radionuclides, cannot be described using a distribution co-efficient.

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Chapter 5

Nuclear Reprocessing-Related Radiocarbon (^{14}C) Uptake into UK Marine Mammals

Abstract

To evaluate the transfer of Sellafield-derived radiocarbon (^{14}C) to top predators in the UK marine environment, ^{14}C activities were examined in stranded marine mammals. All samples of harbour porpoise (*Phocoena phocoena*) obtained from the Irish Sea showed ^{14}C enrichment above background. Mammal samples obtained from the West of Scotland, including harbour porpoise, grey seals (*Halichoerus grypus*) and harbour seals (*Phoca vitulina*) showed ^{14}C enrichment but to a lesser extent. This study demonstrates, for the first time, enriched ^{14}C is transferred through the marine food web to apex predators as a consequence of ongoing nuclear reprocessing activities at Sellafield. Total Sellafield ^{14}C discharge activity 24 months prior to stranding and, in particular, distance of animal stranding site from Sellafield are significant variables affecting individual ^{14}C activity. ^{14}C activities of West of Scotland harbour porpoises suggest they did not forage in the Irish Sea prior to stranding, indicating a high foraging fidelity.

This chapter has been accepted for publication as:

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5.1 Introduction

During reprocessing of nuclear materials at the Sellafield Ltd facility (Figure 5.1A), low-level radioactive waste, including ^{14}C (half-life 5730 years), is discharged to the north-east Irish Sea, primarily as dissolved inorganic carbon (DIC; Begg *et al*., 1992; Cook *et al*., 1995). Dissolved ^{14}C is subject to solution transport and largely dispersed northwards from the Irish Sea by prevailing currents through the North Channel (Gulliver *et al*., 2001) and around the Scottish coastline to the North Sea (Gulliver *et al*., 2004). ^{14}C enters the marine food web via the efficient uptake of soluble ^{14}C in DIC during photosynthesis by primary producing organisms, i.e. phytoplankton (Cook *et al*., 1995, 1998, 2004; Muir *et al*., 2017; Tierney *et al*., 2017). In the UK, Sellafield discharges of ^{14}C have dominated enriched activities in the marine environment. Although Amersham International plc (now GE Healthcare), Cardiff, was an additional source causing localised enriched ^{14}C activities (Cook *et al*., 1998), the ^{14}C discharge activity from this site was minimal between 2000 and 2010 and negligible since 2010 (RIFE, 2016).

Since the early 1990s there have been significant changes in Sellafield ^{14}C discharges to the Irish Sea as described in detail by Muir *et al*. (2017). Briefly, the average discharged ^{14}C activity from 1984 to 1993 was 1.78 Tera Becquerels per year (TBq year^{-1}). An increase in the volume of waste reprocessed and a change in discharge policy in 1994, from an atmospheric route to marine discharge routes, resulted in an increase in marine ^{14}C discharges. The annual discharged activity peaked in 2003 at 16.87 TBq and remained high relative to pre-1994 releases with an average of 7.63 TBq year^{-1} until the end of 2015 (RIFE, 2016; Muir *et al*., 2017).

Recent studies of Sellafield ^{14}C discharges have considered the accumulation of ^{14}C within intertidal environments (Cook *et al*., 2004; Muir *et al*., 2015; Tierney *et al*., 2016) and the biological uptake and transfer of ^{14}C through a major part of the marine food webs of the Irish Sea and West of Scotland (Muir *et al*., 2017; Tierney *et al*., 2017). The latter studies reported enriched activities in a range of marine species occupying the lowest (phytoplankton) to middle-upper (e.g. piscivorous fish) trophic levels and described the trophic transfer of Sellafield-derived ^{14}C previously observed for intertidal organisms (Cook *et al*., 2004). Here we examine ^{14}C activities in marine mammals that occupy the upper trophic levels of the UK marine environment, and which are potentially at risk from increased radioactive dose due to uptake of bioavailable contaminant radionuclides.

Harbour seals (*Phoca vitulina*) are locally resident and typically forage within 40 km of their haul-out sites (Thompson *et al*., 1998). The foraging range of grey seals (*Halichoerus grypus*) can be much larger but individuals will always return to the same breeding site and they are resident to the British Isles (McConnell *et al*., 1999). Less is known about the distribution and behaviour of harbour porpoise (*Phocoena phocoena*) in UK waters, however, population structure analysis of the northeast Atlantic has indicated that there is a subpopulation in British waters (De Luna *et al*., 2012) and ^{137}Cs measurements of their tissues suggest regional residency around the UK (Berrow *et al*., 1998, Watson *et al*., 1999). Resident mammals from the Irish Sea and West of Scotland (defined here as the area located to the north of the North Channel) will be susceptible to ^{14}C enrichment as they spend most or all of their foraging time in waters enriched in ^{14}C and consequently, containing prey species enriched in ^{14}C. In these regions, Sellafield ^{14}C will be transferred through the food chain to marine mammals as has been observed for other species (Muir *et al*., 2017; Tierney *et al*., 2017).

Harbour porpoise, harbour seal and grey seal are generalist predators, although with some dietary specialisations. Overlaps in their diets have been observed in Irish coastal waters where harbour seals and grey seals predate on a number of the same species, as do grey seals and harbour porpoises (Hernandez-Milian, 2014). However, there may be little direct competition between these mammal species as they target prey of different sizes (Hernandez-Milian, 2014). Dietary differences have been observed between porpoise populations in the Irish Sea and the West of Scotland. Harbour porpoises in Irish Sea waters, for example, show a higher presence of pelagic fish such as herring (*Clupea harengu*s) in their diet (Hernandez-Milian, 2014), whereas Scottish coastal harbour porpoises predate more on sandeels (e.g. *Hyperoplus* spp.; Santos *et al*., 2004), although gadoid species are important prey species for both. This difference in diet could be due to prey availability in different environments but it could also indicate a change in diet during the period between studies. Some genetic research has indicated that the Irish Sea harbour porpoise may be a sub-population within the UK population (Anderson *et al*., 2001), although a review of recent literature has found no clear evidence for distinct populations on the west coast of Britain (IAMMWG, 2015) and Fontaine *et al*. (2017) showed that there is a genetic continuum in UK waters.

Figure 5.1A. Map of UK and Ireland indicating study areas (Irish Sea and West of Scotland) and the location of the Sellafield nuclear fuel reprocessing facility.

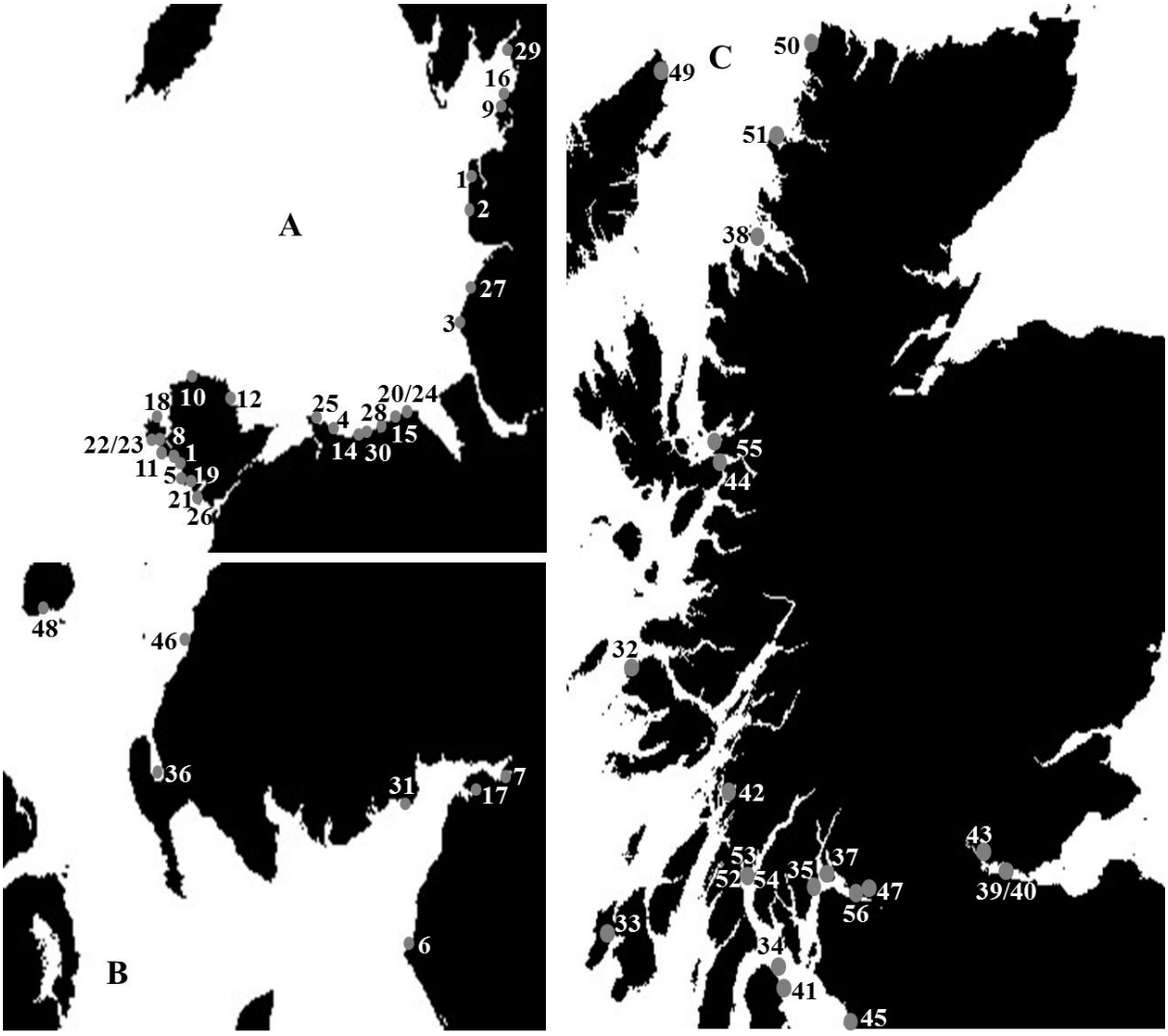

Figure 5.1B. Maps of study areas and stranding locations in the southern Irish Sea (A), the transition area between the Irish Sea and West of Scotland (B) and the West of Scotland with additional sites on the Scottish east coast (C).

The samples described in this study come from animals that were found dead, or died at the stranding site. Studies of ^{137}Cs activities (a radionuclide that was historically discharged to the Irish Sea from Sellafield) in marine mammals stranded in the UK and Ireland have shown that Celtic Sea activities are significantly lower than Irish Sea activities (Berrow *et al*., 1998) and that activities decrease with distance of stranding site from Sellafield (Watson *et al*., 1999). These findings demonstrate that anthropogenic radionuclides are transferred through the food chain to marine mammals and suggest that stranding sites are approximately within the same region in which the animal has been foraging.

The aims of this study were to: 1) evaluate the transfer of Sellafield-derived ^{14}C to top predators in the UK marine environment; 2) examine the spatial distribution of ^{14}C relative to dilution with distance from Sellafield; and 3) determine the effect of temporal changes in Sellafield ^{14}C discharge activities and subsequent transfer through the food chain to marine mammals.

5.2 Methods

Access to the Scottish Marine Animal Stranding Scheme (SMASS) and Cetacean Strandings Investigation Programme (CSIP) sample archives provided the opportunity to consider samples from different mammal species at various locations over a relatively long time-period. The species of interest – harbour porpoise, grey seal and harbour seal – were selected as they represent resident UK marine mammal species, of which a number of samples were available. Muscle tissue samples of stranded mammals from the Irish Sea and the West of Scotland (Figure 5.1B) were identified formally by CSIP and SMASS respectively (Tables 1 and 2). Three time-periods were significant: 1) Pre-1994, when ^{14}C discharges were relatively low, 2) 2001–2004, which encompasses the period of peak ^{14}C discharge, and 3) 2011–2015, to examine contemporary ^{14}C activities in marine mammals. Most of the samples came from these three time-periods, although additional Irish Sea samples were analysed from other years (Tables 5.1 and 5.2). Three samples from the Scottish east coast (Firth of Forth) were also analysed to identify the extent and influence of Sellafield discharges at greater distances from the facility.

Table 5.1. ^{14}C results for mammal samples obtained from the Cetacean Stranding Investigation Programme (CSIP). All samples were from Irish Sea sites.

Sample Number	CSIP Sample Code	Species	Approximate Stranding Location	Year of Stranding	Gross ^{14}C Activity (Bq kg^{-1} C)	Net ^{14}C Activity (Background Corrected; Bq kg^{-1} C)
1	SW1991/71	Harbour Porpoise	Cymyran Bay	1991	280 ± 2	31 ± 2
2	SW1991/135	Harbour Porpoise	Blackpool	1991	302 ± 2	53 ± 2
3	SW1993/34	Harbour Porpoise	Formby Point	1993	351 ± 2	102 ± 2
4	SW2000/131	Harbour Porpoise	Rhos-on-Sea	2000	338 ± 2	89 ± 2
5	SW2000/191	Harbour Porpoise	Rhosneigr	2000	425 ± 2	176 ± 2
6	SW2002/114	Harbour Porpoise	Whitehaven	2002	674 ± 3	425 ± 3
7	SW2002/159	Harbour Porpoise	Port Carlisle	2002	657 ± 3	408 ± 3
8	SW2002/170	Harbour Porpoise	Trearddur Bay	2002	287 ± 2	38 ± 2
9	SW2005/245	Harbour Porpoise	Morecambe	2005	353 ± 2	104 ± 2
10	SW2006/54	Harbour Porpoise	Cemaes Bay	2006	363 ± 2	114 ± 2
11	SW2006/308A	Harbour Porpoise	Trearddur Bay	2006	315 ± 2	66 ± 2
12	SW2008/37	Harbour Porpoise	Dulas Bay	2008	356 ± 2	107 ± 2
13	SW2008/60	Harbour Porpoise	Blackpool	2008	365 ± 2	116 ± 2
14	SW2010/133	Harbour Porpoise	Abergele	2010	609 ± 3	360 ± 3
15	SW2010/152	Harbour Porpoise	Rhyl	2010	489 ± 3	240 ± 3
16	SW2010/233	Harbour Porpoise	Morecambe	2010	608 ± 3	359 ± 3
17	SW2010/338	Harbour Porpoise	Anthorn	2010	308 ± 2	59 ± 2
18	SW2011/35	Harbour Porpoise	Holyhead	2011	429 ± 2	180 ± 2
19	SW2011/109	Harbour Porpoise	Porth Cwyfan	2011	395 ± 2	146 ± 2
20	SW2012/195	Harbour Porpoise	Rhyl	2012	286 ± 2	37 ± 2
21	SW2013/45	Harbour Porpoise	Aberffraw	2013	296 ± 2	47 ± 2
22	SW2013/273	Harbour Porpoise	Porth Dafarch	2013	524 ± 2	275 ± 2
23	SW2013/327	Harbour Porpoise	Porth Dafarch	2013	315 ± 2	66 ± 2
24	SW2013/381	Harbour Porpoise	Prestatyn	2013	359 ± 2	110 ± 2
25	SW2014/86	Harbour Porpoise	Landudno	2014	428 ± 2	179 ± 2
26	SW2014/272	Harbour Porpoise	Newborough	2014	288 ± 2	39 ± 2
27	SW2014/475	Harbour Porpoise	Ainsdale	2014	326 ± 2	77 ± 2
28	SW2015/6	Harbour Porpoise	Rhyl	2015	285 ± 2	36 ± 2
29	SW2015/123	Harbour Porpoise	Carnforth	2015	325 ± 2	76 ± 2
30	SW2015/224	Harbour Porpoise	Abergele	2015	324 ± 2	75 ± 2

Table 5.2. ^{14}C results for mammal samples obtained from the Scottish Marine Animal Stranding Scheme (SMASS). All samples were from the West of Scotland with the exception of one from the Irish Sea and three from the Scottish east coast.

Sample Number	SMASS Sample Code	Species	Approximate Stranding Location	Year of Stranding	Gross ^{14}C Activity (Bq kg^{-1} C)	Net ^{14}C Activity (Background Corrected; Bq kg^{-1} C)
31	M1970/92	Harbour Porpoise	Southerness (Irish Sea)	1992	372 ± 2	123 ± 2
32	M0105/93	Harbour Porpoise	Isle of Mull	1993	255 ± 1	6 ± 1
33	M1106/93	Harbour Porpoise	Islay	1993	257 ± 1	8 ± 1
34	M210/03	Harbour Porpoise	Dunoon	2003	403 ± 2	154 ± 2
35	M197/03	Harbour Porpoise	Isle of Arran	2003	329 ± 2	80 ± 2
36	M186/04	Harbour Porpoise	Stranraer	2004	374 ± 2	125 ± 2
37	M228/04	Harbour Porpoise	Loch Long	2004	368 ± 2	119 ± 2
38	M241/11	Grey Seal	Gruinard river	2011	263 ± 1	14 ± 1
39	M62/12A	Harbour Porpoise	Bo' ness (east coast)	2012	262 ± 1	13 ± 1
40	M87/12	Harbour Porpoise	Bo' ness (east coast)	2012	264 ± 1	15 ± 1
41	M173/12	Harbour Porpoise	Isle of Arran	2012	309 ± 2	60 ± 2
42	M082/13	Harbour Seal	Loch Melfort	2013	260 ± 1	11 ± 1
43	M092/13	Harbour Porpoise	Alloa (east coast)	2013	253 ± 1	4 ± 1
44	M198/13	Harbour Seal	Isle of Skye	2013	254 ± 1	5 ± 1
45	M5/14	Harbour Seal	Troon	2014	284 ± 2	35 ± 2
46	M68/14	Harbour Porpoise	Girvan	2014	238 ± 1	-11 ± 1
47	M134/14	Harbour Porpoise	River Clyde	2014	294 ± 2	45 ± 2
48	M139/14	Harbour Porpoise	Kintyre	2014	398 ± 2	149 ± 2
49	M147/14	Harbour Porpoise	Isle of Lewis	2014	258 ± 2	9 ± 2
50	M279/14	Harbour Porpoise	Kinlochbervie	2014	242 ± 2	-7 ± 2
51	M319/14	Harbour Porpoise	Clacktoll	2014	254 ± 1	5 ± 1
52	M378/14	Harbour Seal	Loch Fyne	2014	262 ± 2	13 ± 2
53	M384/14	Grey Seal	Loch Fyne	2014	271 ± 2	22 ± 2
54	M385/14	Grey Seal	Loch Fyne	2014	265 ± 1	16 ± 1
55	M137/15	Harbour Seal	Isle of Skye	2015	259 ± 2	10 ± 2
56	M147/15	Harbour Seal	River Clyde	2015	254 ± 2	5 ± 2

The analytical techniques employed are described in detail in Muir *et al*. (2017) and are briefly summarised here. Muscle tissue samples from each organism were freeze-dried and approximately 15 mg were combusted (850^{o}C) in sealed quartz tubes, according to the method of Vandeputte *et al*. (1996) to liberate CO_2 gas. CO_2 was cryogenically purified (under vacuum) and converted to graphite (Slota *et al*., 1987) prior to $^{14}C/^{13}C$ isotope ratio measurement by accelerator mass spectrometry (AMS). Sub-samples of CO_2 were collected to determine the $\delta^{13}C$ value ($^{13}C/^{12}C$ stable isotope ratio) for calibration of natural fractionation of measured ^{14}C. Reported AMS fraction modern results were converted to specific activities (Bq kg^{-1} C) using the regime described by Mook and van der Plicht (1999). Error bars are omitted from figures, as analytical uncertainties for AMS measurements at SUERC are typically less than 0.5% of the measured activity, and therefore indistinguishable in measured values. Statistical analyses and modelling were conducted using the software package R (R Development Core Team, 2016). Generalised least squares (GLS) regression models were used to identify significant variables and model fit was compared using the corrected Akaike information criterion (AICc; Venables and Riley, 2002).

Due to natural production of ^{14}C and the legacy of ^{14}C from atmospheric testing of atomic weapons during the 1950s and 1960s, a baseline (or background) activity was quantified to determine enriched activities resulting from Sellafield discharges. Cook *et al*. (1998) defined the UK ^{14}C coastal marine background as 248 ± 1 Bq kg^{-1} C from west coast of Ireland samples that are free of UK coastal influences, i.e. Sellafield radionuclide discharges. Tierney *et al*. (2016) presented a new, but near-identical, UK ^{14}C background activity of 249 ± 1 Bq kg^{-1} C which has been used in subsequent studies (Muir *et al*., 2017; Tierney *et al*., 2017) and is used here.

5.3 Results

Analytical results for samples obtained from CSIP and SMASS are listed in Tables 5.1 and 5.2, respectively. Of the 56 marine mammal samples analysed, three were from grey seals, six from harbour seals and 47 from harbour porpoises. Two samples (46 and 50) were measured with ^{14}C activities below that of the current UK coastal marine background. These came from porpoises stranded in the West of Scotland in 2014 (238 ± 1 Bq kg^{-1} C and 242 ± 1 Bq kg^{-1} C). The highest measured (gross) activities were from two porpoises (samples 6 and 7) that stranded in the Irish Sea in 2002 (674 ± 3 Bq kg^{-1} C and 657 ± 3 Bq

kg^{-1} C). One harbour seal sample and two grey seal samples (52, 53 and 54) from animals that died at approximately the same time in Loch Fyne (West of Scotland) showed similar ^{14}C activities (262 ± 1 Bq kg^{-1} C, 271 ± 1 Bq kg^{-1} C and 265 ± 1 Bq kg^{-1} C), respectively. Conversely, two young male harbour porpoises (samples 22 and 23) that stranded at Porth Dafarch (North Wales) on the Southern Irish Sea coastline at a similar time had a relatively large difference in measured activity (524 ± 2 Bq kg^{-1} C and 315 ± 2 Bq kg^{-1} C). The average ^{14}C activity across all Irish Sea samples was 388 Bq kg^{-1} C, compared to a significantly lower ^{14}C activity of 285 Bq kg^{-1} C for West of Scotland samples. Three samples from the Scottish east coast (39, 40 and 43) also show enriched ^{14}C activities (253 ± 1, 262 ± 1 and 264 ± 1 Bq kg^{-1} C).

No seal samples were obtained for the Irish Sea area and the number of seal samples was low overall, relative to that of harbour porpoise, resulting in a large activity difference between the ranges observed for seal (254–284 Bq kg^{-1} C) and porpoise (238–674 Bq kg^{-1} C) ^{14}C activities. As there was no significant difference between seal and porpoise ^{14}C activity in the West of Scotland, these species were grouped for statistical analysis.

A number of variables were considered to explain the measured ^{14}C activities, including distance (measured as distance from Sellafield by sea in km), sex, age class (neonate, juvenile, sub-adult and adult), level of decomposition (freshly dead, slight and moderate decomposition), month of stranding and year of stranding. The data were explored prior to statistical analyses and linear model assumptions checked. As correlation in the data residuals was detected, generalised least squares (GLS) regression was used with a simple correlation structure (AR1) and model descriptions, and AICc scores are given in Table 5.3. Initial model fitting of ^{14}C activity found the best fit (lowest AICc score) when only including the predictor variable distance (Model 1). However, the relationship between sample activity and distance was not significant ($p > 0.01$). Distance appears to have an exponential influence on activity as stranding site gets closer to Sellafield (Figure 5.2). Model fitting of log-transformed ^{14}C activity found distance significantly ($p < 0.001$) affected ^{14}C activity and the model with the lowest AICc score also included year, despite this variable having little significance ($p > 0.01$; Model 2). It is likely that year improved model fit due to the temporal changes in Sellafield ^{14}C discharges having some effect on individual ^{14}C activities, although this is not obvious in Figure 5.3. A new variable was considered describing discharge activity prior to stranding (pDischarge), where pDischarge is the sum of total monthly ^{14}C activities discharged from Sellafield (a) for a

number of months (n) prior to the month of stranding (s; Equation 1). Periods of 6, 12, 24 and 36 months were considered and 12 (Model 3) and 24 months (Model 4) were found to improve model fit, however, pDischarge had little significance (p >0.01).

Equation 1

$$pDischarge = \sum_{i=s}^{n} a_i$$

Sellafield discharges will not reach the West of Scotland environment immediately. Estimates for transit times of other highly soluble radionuclides discharged from Sellafield (^{134}Cs, ^{137}Cs and ^{99}Tc) range from 3 to 18 months (Jefferies *et al*., 1973, Kershaw and Baxter, 1995, Kershaw *et al*., 2004). To account for transit time in calculating pDischarge for West of Scotland samples, a delay factor (d) was used (Equation 2). Although a number of delay factors were considered, a factor of 12 months was statistically significant (p <0.01), and improved model fit when included with distance (p <0.0001; Model 5). A delay factor of 12 months meant pDischarge for West of Scotland samples was the total ^{14}C discharge activity from 12 to 36 months prior to stranding.

Equation 2

$$pDischarge = \sum_{i=s-d}^{n} a_i$$

Distance alone (Model 6) did not improve model fit and although pDischarge was significant, there is no obvious correlation between ^{14}C activity and pDischarge (Figure 5.4) and pDischarge alone (Model 7) did not improve the model fit. Therefore, the overall best model fit for mammal ^{14}C activity included the predictor variables of: distance of stranding from Sellafield and total Sellafield ^{14}C discharge activity 24 months prior to stranding, including a 12-month delay for West of Scotland animals (Model 5). For every kilometre increase away from Sellafield, this model predicts an estimated 0.3% decrease in sample activity. For every TBq increase in discharged ^{14}C activity during the 24 months prior to stranding, the model predicts an estimated 6.5% increase in sample activity. The combined effect of distance and prior Sellafield discharges on sample ^{14}C activity is illustrated in Figure 5.5 where distance is normalised to pDischarge and the scatter again indicates an exponential relationship.

Table 5.3. Statistical model descriptions. The AICc scores provide a comparative measurement of goodness of fit where lower values indicate a better model fit.

Model No.	Description	AICc
Model 1	Best model fit without log-transforming ^{14}C activity. Model included the variable distance ($p > 0.01$) but was not deemed significant.	644.6
Model 2	Log-transformed ^{14}C activity with variables: distance from Sellafield ($p < 0.001$) and year of stranding ($p > 0.01$),	152.6
Model 3	Log-transformed ^{14}C activity with variables: distance from Sellafield ($p < 0.0001$) and pDischarge 12 months prior to stranding ($p > 0.01$).	146.1
Model 4	Log-transformed ^{14}C activity with variables: distance from Sellafield ($p < 0.0001$) and pDischarge 24 months prior to stranding ($p > 0.01$).	143.9
Model 5	Log-transformed ^{14}C activity with variables: distance from Sellafield ($p < 0.0001$) and pDischarge 24 months prior to stranding including delay factor of 12 months for West of Scotland mammals ($p < 0.01$).	139.2
Model 6	Log-transformed ^{14}C activity with variable distance from Sellafield only ($p < 0.0001$).	147.2
Model 7	Log-transformed ^{14}C activity with variable pDischarge only ($p < 0.01$).	166.0

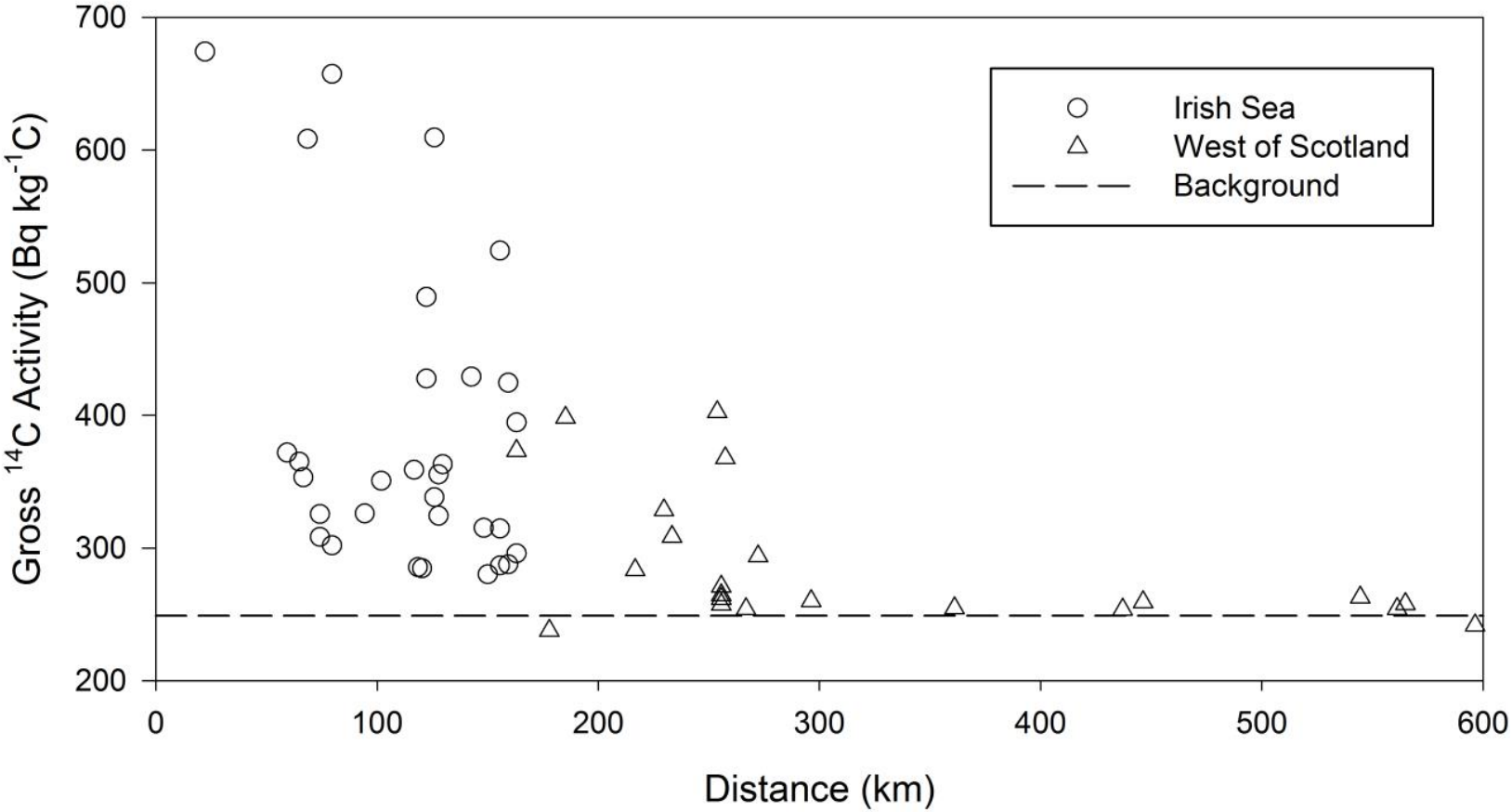

Figure 5.2. Sample ^{14}C activities as a function of distance of stranding site from Sellafield by sea (Scottish east coast samples have been omitted for clarity).

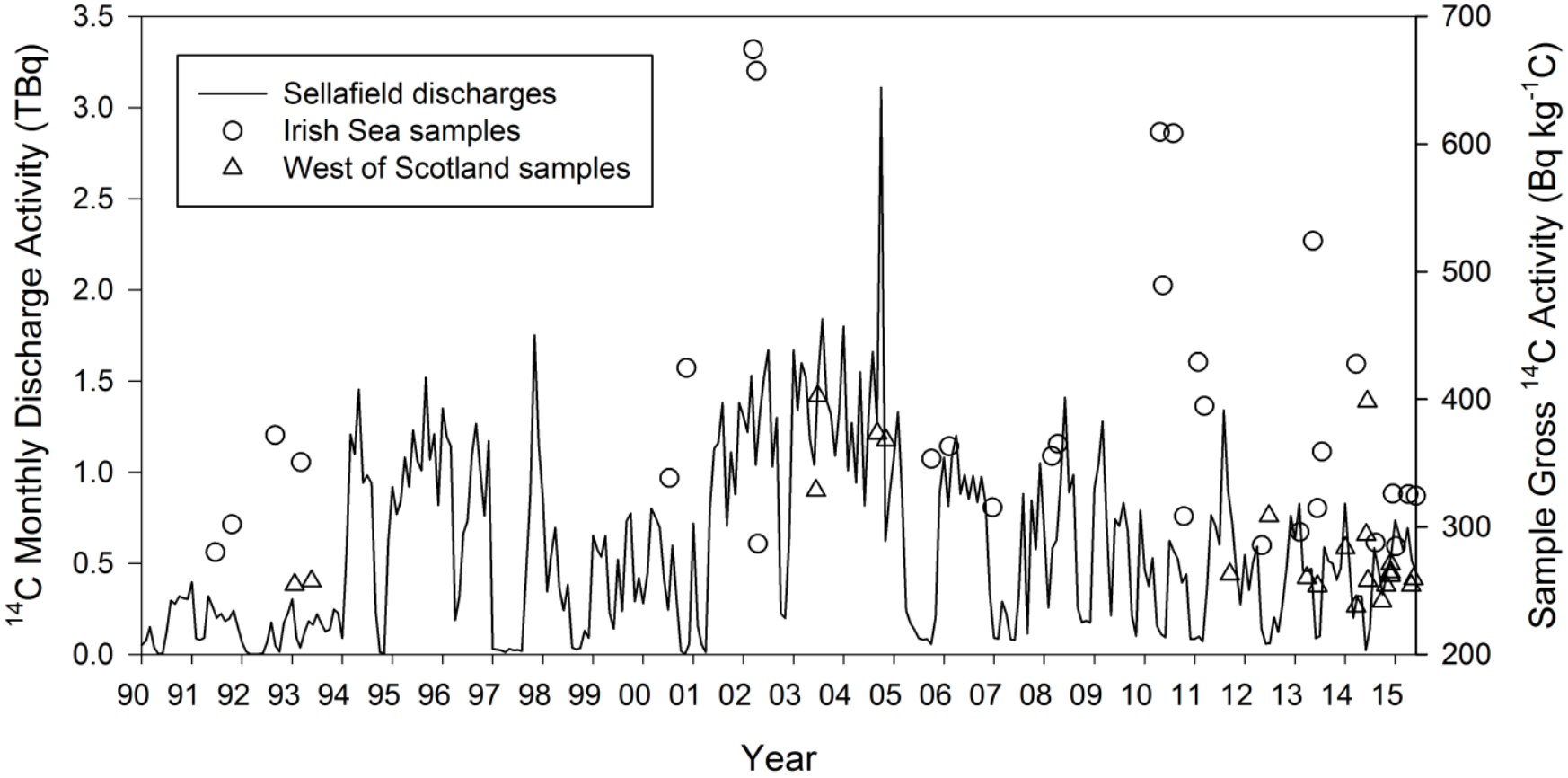

Figure 5.3. Sellafield total monthly ^{14}C discharges made to the Irish Sea from January 1990 to June 2015 and sample ^{14}C activities.

5.4 Discussion

The two West of Scotland samples (46 and 50) with below UK coastal marine ^{14}C background activities (238 ± 1 Bq kg^{-1} C and 242 ± 2 Bq kg^{-1} C) were from young female porpoises that stranded hundreds of kilometres apart (approximately 178 km and 596 km from Sellafield respectively). Similar activities were observed in phytoplankton and zooplankton in the West of Scotland (Tierney *et al*., 2017). It is not clear why these ^{14}C activities would be below this background value, however, the depleted plankton activities were linked to a possible source of older water, possibly derived from upwelling of deep Atlantic water or another Atlantic source, reducing ambient ^{14}C activities (Tierney *et al*., 2017). Natural ^{14}C activities are not homogenous and the cited UK coastal marine ^{14}C background activity does not represent the "oceanic background" for the entire north-east Atlantic. This may vary as ^{14}C produced by atomic weapon testing decays in different hydrographic and biogeochemical settings (Scourse *et al*., 2012). The lower activities could result from the animals previously inhabiting a region with a lower ambient ^{14}C activity before stranding at these sites.

The relatively high ^{14}C activities (674 ± 3 and 657 ± 3 Bq kg^{-1} C) observed in harbour porpoises stranded close to Sellafield in 2002 (samples 6 and 7) coincides with the period of peak ^{14}C discharges. Although peak ^{14}C discharge occurred in 2003 (17 TBq), cumulative increases in ^{14}C discharge were made to the Irish Sea in both 2001 (9.5 TBq) and 2002 (13 TBq). Similarly, higher activities (608 ± 3 Bq kg^{-1} C and 609 ± 3 Bq kg^{-1} C) were measured in two harbour porpoises that stranded in different areas of the Irish Sea in 2010 (samples 14 and 16). Although the 2010 annual discharge (4.4 TBq) was low relative to the peak discharges, the 2009 annual discharge (8.2 TBq) was the highest between 2006 and 2015. However, a porpoise (sample 17) that stranded relatively close to Sellafield in 2010 (74 km away) had a comparatively low activity (308 ± 2 Bq kg^{-1} C). This individual died from starvation and an extended period of limited foraging with little or no food intake from the eastern Irish Sea may help explain this individual's anomalously low ^{14}C activity.

It is reasonable to assume that samples obtained from animals of the same or similar species that stranded in the same location at the same time of year, would have comparable ^{14}C activities. This was observed in three seal samples (52, 53 and 54) from Loch Fyne (West of Scotland; 262 ± 1 Bq kg^{-1} C, 271 ± 1 Bq kg^{-1} C and 265 ± 1 Bq kg^{-1} C). The fact that two porpoise samples (22 and 23) from Porth Dafarch (North Wales) had significantly

different activities (524 ± 2 Bq kg^{-1} C and 315 ± 2 Bq kg^{-1} C) illustrates the difficulty in making assumptions based on stranding location alone. Animals that inhabit different areas might strand in the same area due to a number of variables including changes in water masses, wind patterns, and bloating of animal carcasses prior to stranding. However, diet source will directly affect the individual's ^{14}C activity. Studies of shark age, using the radiocarbon bomb peak (from atomic weapons testing), found that changes in diet could affect shark vertebrae ^{14}C activity (Campana *et al*., 2002). Sharks feeding on longer-lived species during the bomb peak could have a relatively lower ^{14}C activity because of integration with lower activities from before the bomb peak (Campana *et al*., 2002; Kerr *et al*., 2006). Integration of higher ^{14}C activities from Sellafield discharges have also been linked to higher activities in longer-lived species at specific sites in the Irish Sea (Muir *et al*., 2017). Of the two Porth Dafarch porpoise samples, the higher ^{14}C activity came from a juvenile porpoise, whereas the lower activity was from a neonate. The ^{14}C activity of the neonatal porpoise is likely a result of transfer from mother to calf. It could be inferred, therefore, that its mother had been foraging in an area of lower ambient activity relative to the sampled juvenile. It is equally possible that the mother of the neonatal porpoise had a lower ^{14}C activity due to a longer integration period covering a previous period of lower prey ^{14}C activity and this was transferred to the calf.

During data analysis, species type did not have an impact on sample ^{14}C activity. However, harbour seal and grey seal samples were only available from the West of Scotland where there was little observed variation in ^{14}C activities relative to Irish Sea mammals, and concurs with the relative homogeneity in ^{14}C activities of other marine species in this area (Tierney *et al*., 2017). In order to determine whether diet and life history influence mammal ^{14}C activities between species, it would be necessary to analyse seal samples from the Irish Sea.

Across all the data, several other variables including sex, age class (neonate, juvenile, sub-adult and adult) and level of decomposition (freshly dead, slight and moderate decomposition), showed no significance with ^{14}C activity. However, distance of stranding site from Sellafield and the Sellafield ^{14}C discharge activity prior to stranding (pDischarge) were significant. The best model fit predicted that for every 1 km increase in distance away from Sellafield there would be an estimated 0.3% decrease in mammal ^{14}C activity. This is significant as the samples analysed in this study came from mammals that stranded in the range of 10–1000 km from Sellafield. It indicates that stranding site is a reasonable

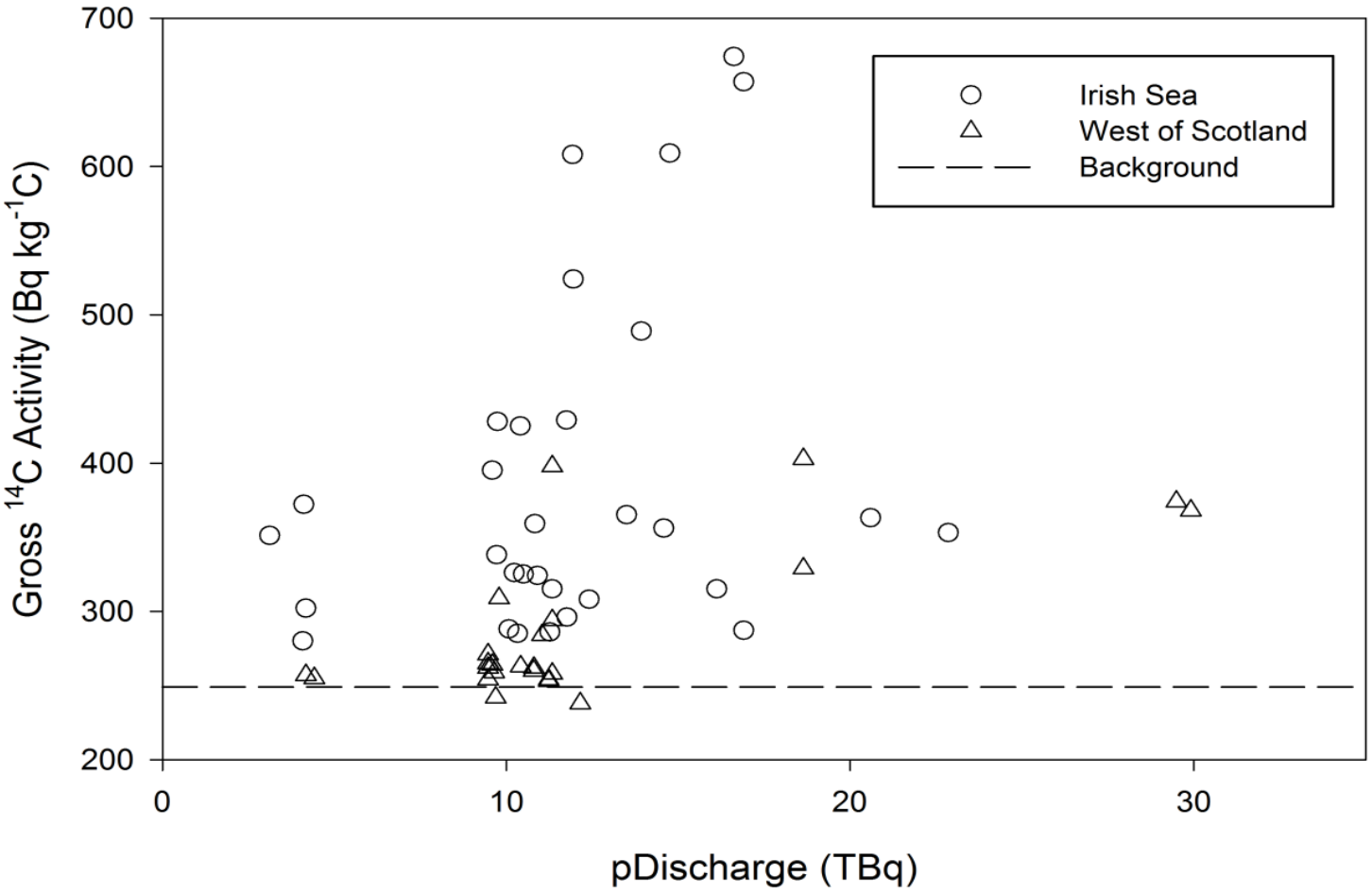

Figure 5.4. Sample ^{14}C activities as a function of Sellafield ^{14}C discharge activity for 24 months prior to stranding, including a 12-month delay factor for West of Scotland samples.

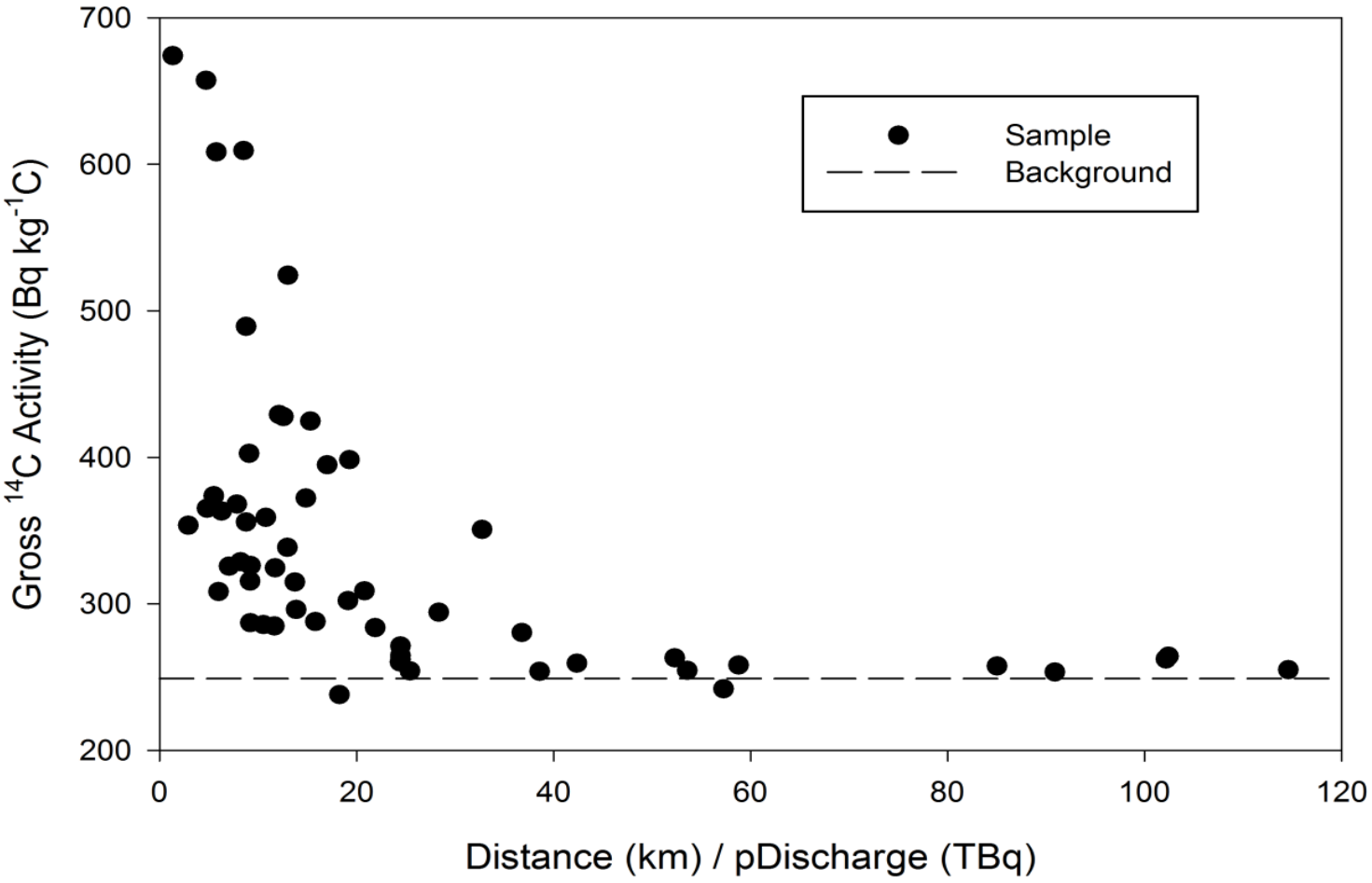

Figure 5.5. Sample ^{14}C activity as a function of stranding distance from Sellafield, normalised by the discharge activity for the 24 months prior to individual stranding (note that no delay factor for West of Scotland samples is included here).

approximation for the area an individual has been foraging in, as ^{14}C activities in the UK marine environment reduce with distance from Sellafield (Begg *et al*., 1992; Cook *et al*., 1998, 2004; Muir *et al*., 2015; Tierney *et al*., 2016; Muir *et al*., 2017; Tierney *et al*., 2017). Within the Irish Sea and, in particular, at stranding distances of less than 200 km from Sellafield, there was a wide range of ^{14}C activities (280–674 Bq kg^{-1} C). At distances greater than 200 km a general tail of decreasing ^{14}C activity is apparent and a distinct reduction in maximum activity exists between Irish Sea and West of Scotland samples. Three samples from the Scottish east coast show slight enrichments above ^{14}C background activity (253–264 ± 1 Bq kg^{-1} C). This could indicate the long distance dispersion of ^{14}C from Sellafield to the North Sea, as has been noted before (Cook *et al*., 1998; Gulliver *et al*., 2004). The reduction in ^{14}C activity with distance from Sellafield is due to dilution and subsequently lower activities within prey species (Tierney *et al*., 2017) as discussed below.

The best model fit also predicted that for every 1 TBq increase in total Sellafield ^{14}C discharge activity for the period of 24 months prior to stranding, mammal ^{14}C activity would increase by an estimated 6.5%. This confirms that Sellafield is the source of ^{14}C enrichment in these samples. Furthermore, it also indicates the complex nature of ^{14}C transfer to these animals through the food web and shows the persistence of enriched ^{14}C within the marine environment, despite dispersion and dilution. Adding a delay factor of 12 months for West of Scotland samples improved the overall model fit. It suggests that the sampled West of Scotland mammals have spent little or no time foraging in the Irish Sea during the 12 months prior to stranding. This is expected of harbour seals as they typically only forage within 40 km of their haul-out site (Thomson *et al*., 1998). However, the number of harbour seal samples analysed was low (6) so this increased significance is unlikely to be attributable to these samples alone. In addition, few grey seal samples were analysed (3), therefore it is likely that the increased model significance is proportionally weighted toward the porpoise samples, which made up the bulk of the samples analysed (47). By removing the seal samples from the model fitting process, a similar level of significance for pDischarge ($p < 0.01$) was found. The model fit suggests that the sampled West of Scotland porpoises fed mainly in areas *other* than that of the Irish Sea for (at least) 12 months prior to stranding. This indicates a high foraging fidelity for harbour porpoises in the West of Scotland.

Herring, sandeel and gadoid species such as haddock (*Melanogrammus aeglefinus*) and whiting (*Merlangius merlangus*) are important prey for harbour porpoise (Santos *et al*.,

2004, Hernandez-Milian, 2014). Herring activity (from a bulk sample) in the eastern Irish Sea in 2014 was reported at 274 ± 1 Bq kg^{-1} C, sandeel 314 ± 1 Bq kg^{-1} C and Irish Sea haddock ranged between 293-469 Bq kg^{-1} C (Muir *et al*., 2017). The average ^{14}C activity of the six Irish Sea porpoise samples from animals that stranded between 2014 and 2015 was 329 Bq kg^{-1} C (range 288–428 Bq kg^{-1} C) and agrees well with the ^{14}C activities of their prey species. This is expected as ^{14}C is transferred through the food web without any bioaccumulation or concentration effect. Measurements of West of Scotland fish demonstrated ^{14}C activity ranges of 282–284 Bq kg^{-1} C in herring, 286–296 Bq kg^{-1} C in haddock, and 288–413 Bq kg^{-1} C in whiting (Tierney *et al*., 2017). These activities fit reasonably well with the range of porpoise and seal activities between 2014 and 2015 porpoise (254–398 Bq kg^{-1} C), after exclusion of the two individuals with below-background activities. The average mammal ^{14}C activity of these ten samples, 280 Bq kg^{-1} C, is at the lower end of the prey species activity range. However, the mammal samples come from a much wider area, including north of the fish sample sites, where ^{14}C activities in other benthic species are lower (Tierney *et al*., 2017). It is apparent that trophic transfer of enriched ^{14}C from prey species is the cause for enriched activities found in mammals. The significant relationship that exists between Sellafield ^{14}C discharges and mammal ^{14}C activity, and the comparable activities between predator and prey, demonstrate the transfer pathway in its entirety as a trophic level flow of ^{14}C from source to top marine predators.

5.5 Conclusions

Enriched ^{14}C activities were found in almost all marine mammal samples from the west coast of the British Isles. The highest activities were from harbour porpoises that stranded within the Irish Sea, although enriched ^{14}C activities were also observed in the West of Scotland and in three samples from the Scottish east coast. ^{14}C activities vary greatly both temporally and spatially. They correlate significantly with: 1) the distance the animal stranded from the Sellafield nuclear fuel reprocessing facility; and 2) the total ^{14}C activity discharged from Sellafield to the Irish Sea for a period of 24 months prior to stranding.

West of Scotland marine mammal ^{14}C activities correlate significantly with discharges made between 12 and 36 months prior to the animal stranding. This indicates the time taken for Sellafield ^{14}C discharges to be transported to the West of Scotland environment and become fully integrated in prey species. The model fit also suggests that West of

Scotland harbour porpoises did not forage in the Irish Sea and have a high foraging fidelity to the West of Scotland.

^{14}C activities in samples from 2014 and 2015 are similar to ^{14}C activities measured in typical prey species showing that transfer of enriched ^{14}C from prey to predator occurs without any concentration or bioaccumulation effect. Although the ^{14}C activities presented in this study do not pose any radiological risk to the individual, it is clear that ^{14}C enrichment in marine mammals result from ^{14}C transfer from prey species, and that distance and discharge activity from Sellafield are key factors in determining an individual's muscle ^{14}C activity.

Sellafield is one of a number of facilities that continue to release low-level radioactive material, such as ^{14}C, into the marine environment. This study demonstrates, for the first time, the transfer of nuclear industry derived, ^{14}C through the entire marine food web to top predators, and highlights the necessity for continual monitoring of the fate of ^{14}C and other bioavailable radionuclides in marine ecosystems. Future work includes measuring ^{14}C concentrations in seals from the Irish Sea and addressing differences in ^{14}C transfer in relation to dietary preferences.

5.6 References

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Chapter 6
Modelling Marine Trophic Transfer of Radiocarbon (^{14}C) from a Nuclear Facility

Abstract

Sellafield marine discharges of ^{14}C are the largest contributor to the global collective dose from the nuclear fuel industry. As such, it is important to understand the fate of these discharges beyond the limitations and scope of empirical analytical investigations for this highly mobile radioactive contaminant. Ecopath with Ecosim (EwE) is widely used to model anthropogenic impacts on ecosystems, such as fishing, although very few EwE studies have modelled the fate of bioavailable contaminants. This work presents, for the first time, a spatial-temporal ^{14}C model utilising recent developments in EwE software to predict the ecological fate of anthropogenic ^{14}C in the marine environment. The model predicted observed trends in ^{14}C activities between different species and through time. It also provided evidence for the integration of Sellafield ^{14}C in species at higher trophic levels through time.

This chapter has been submitted for publication as:

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6.1 Introduction

Understanding the ecological fate of anthropogenic radionuclides is necessary to determine any potentially hazardous consequences to the environment and to human populations. Although empirical studies are essential, they are often time-consuming, costly and impractical to conduct, particularly if basic information is required quickly (e.g. after accidental releases of radioactive material) or, if radioactive contamination is spread over a large area. Computer modelling provides an additional tool which can be both time- and cost-effective. The ecosystem modelling software suite, Ecopath with Ecosim (EwE) (Christensen and Walters 2004), has undergone recent developments that aid its ability to model the ecological fate of environmental contaminants spatially. EwE has previously been used to model non-radioactive contaminants such as methyl-mercury in the Faroe Islands marine ecosystem (Booth and Zeller 2005), chemical warfare agents in the Baltic Sea (Niiranen *et al*., 2008; Sanderson *et al*., 2010), polycyclic aromatic hydrocarbons (PAHs) in the Arctic (Larsen *et al*., 2016) and polychlorinated biphenyls (PCB) and mercury in the Great Lakes (McGill *et al*., 2017). EwE has also been used to model radioactive contaminants, including a hypothetical release of radiocarbon (^{14}C) in the Baltic Sea (Sandberg *et al*., 2007) and radiocaesium (^{137}Cs) in a simple, coastal marine ecosystem model for Fukushima (Walters and Christensen 2017). Many of these studies considered temporal change in contaminant activity but not spatial variation. The EwE approach is appealing for modelling bioavailable contaminants, due primarily to its ease of use. There are over 400 unique EwE models published, making it the most extensively applied tool for modelling marine and aquatic ecosystems (Colleter *et al*., 2015). The extensive coverage of published EwE models also means that models may already exist for a specific ecosystem in which an environmental contaminant is present, or subject to a recent contamination event, and can be adapted for this purpose.

There are four components to EwE: 1) Ecopath, which describes a static, mass-balanced ecosystem (Polovina, 1984); 2) Ecosim, a time-dynamic simulation module allowing for temporal changes and impacts to an ecosystem to be investigated (Walters *et al*., 1997); 3) Ecospace, where ecosystem changes can be explored both spatially and temporally (Walters *et al*., 1999); and 4) Ecotracer which traces contaminants through the ecosystem (Walters and Christensen 2017). While Ecosim/Ecospace solve biomass dynamic equations, Ecotracer simultaneously models contaminant flow and/or accumulation in the ecosystem, described in Ecopath. Ecotracer and the equations it utilises are described in

full in Walters and Christensen (2017). The development of the spatial-temporal EwE framework (Steenbeek *et al*., 2013) allows physical changes to occur in the Ecospace environment through time. As environmental contamination is typically non-ubiquitous and non-static, this is an appropriate development to consider for contaminant models where contaminant concentrations in the environment are both temporally and spatially variable.

In recent decades, several studies have accumulated a large body of data regarding the fate of ^{14}C discharged by the Sellafield nuclear fuel reprocessing facility in Cumbria, UK, to the marine environment (Begg *et al*., 1992; Cook *et al*., 1995, 1998, 2004; Gulliver *et al*., 2001, 2004; Mackenzie *et al*., 2004, Muir *et al*., 2015, 2017; Tierney *et al*., 2016, 2017a, 2017b). The most recent work has focussed on detailing the ecosystem uptake of ^{14}C in the Irish Sea (Muir *et al*., 2017), and the West of Scotland (Tierney *et al*., 2017a) marine environments, and has established a time-series of ^{14}C activities in marine mammals along the UK coastline (Tierney *et al*., 2017b). Sellafield discharges ^{14}C as low-activity waste effluent via pipelines to the Irish Sea in the dissolved inorganic phase, which is rapidly incorporated into the marine dissolved inorganic carbon (DIC) pool (Begg *et al*., 1992; Cook *et al*., 1995). In this manner, Sellafield ^{14}C spreads throughout the Irish Sea and is largely dispersed northward through the North Channel to the West of Scotland marine environment by prevailing currents (Gulliver *et al*., 2001). Whilst contemporary environmental releases of ^{14}C from Sellafield do not pose any direct radiological risk to critical consumer groups near Sellafield (Muir *et al*., 2017), releases of ^{14}C are still highly significant. ^{14}C has a long half-life (5730 years), is environmentally mobile, highly bioavailable and marine discharges are the largest contributor to the UK, European and global collective dose from Sellafield (Nuclear Decommissioning Authority, 2016).

The aim of this study was to construct an EwE contaminant tracing model for Sellafield ^{14}C in the UK marine environment, the 'Sellafield model', and to test it, primarily, using recent data compiled in Muir *et al*. (2017) and Tierney *et al*. (2017a, 2017b). The development of the Sellafield model allows an EwE model to be tested, for the first time, on its ability to accurately predict the spatial ecosystem uptake and fate of radionuclides discharged routinely to the marine environment. The unique biogeochemical properties of ^{14}C, in being identical in its behaviour to stable carbon on an ecosystem level, coupled with its long half-life, make it an 'ideal' contaminant with which to evaluate the performance

and applicability of the EwE model and Ecotracer utility for radioactive contamination scenarios.

6.2 Methods

6.2.1 Ecopath input

In EwE, functional groups are either specific species or a group of species deemed to have sufficiently similar functionality for the purposes of the model (Heymans *et al*., 2016). The productivity of each functional group is defined in Ecopath by the equation:

$$P_i = Y_i + B_i.M2_i + E_i + BA_i + P_i.(1 - EE_i)$$

where for group i: P_i is the total production rate, Y_i is the total fishery catch rate, B_i is the biomass, $M2_i$ is the total predation rate, E_i is the net migration rate (emigration–immigration), BA_i is the biomass accumulation rate and EE is the ecotrophic efficiency of the group (Christensen and Walters 2004). Ecotrophic efficiency is the proportion of a group's production that is explained in the model and this cannot exceed 1. Functional groups require a number of input parameters to satisfy the Ecopath mass balance equation. Values for biomass (B), annual production/biomass (P/B) and either annual consumption/biomass (Q/B) or production/consumption (P/Q) are typical inputs.

As Sellafield discharges ^{14}C into the Irish Sea, a mass balanced EwE model developed by Lees and Mackinson (2007) that describes the Irish Sea ecosystem in the early 1970s was used as the foundation for the Sellafield model. However, aspects of this model were either beyond the complexity required for the Sellafield model or not descriptive enough and a number of changes were made. The Lees and Mackinson Irish Sea model contains a total of 53 functional groups which was reduced to 43 in the Sellafield model as discussed below.

Three model groups, cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus*) and plaice (*Pleuronectes platessa*), were separated into two age classes (adult and juvenile). These separations were not necessary for this study and these species were combined into single species groups in the Sellafield model. Muir *et al*. (2017) and Tierney *et al*. (2017a) describe ^{14}C activities in three fish species; dab (*Limanda limanda*), ling (*Molva molva*) and herring (*Clupea harengus*), which are not individually specified in the Irish Sea model.

Using species information described in Lees and Mackinson (2007), dab was separated from the "medium flatfish" functional group, ling extracted from "other large demersals", and herring from "other small pelagic planktivorous fish". The functional groups, small, medium and large flatfish were combined into the singular "other flatfish" group. Likewise, a single functional group called "other demersals" was created by combining bass, seatrout, gurnards, mullet, other large demersals, other large gadoids, other small demersals and other small gadoids. The Irish Sea model contained four zooplankton groups (herbivorous, omnivorous, carnivorous and gelatinous) which were also combined to form a single zooplankton group. Where groups were combined, biomass values were summed and other input parameters from Lees and Mackinson (2007) were calculated as a proportion of the biomasses of the previously existing groups. Where new groups were extracted, biomasses and other input parameters were taken as described in Lees and Mackinson (2007).

Tierney *et al*. (2017b) describe ^{14}C activities in 3 marine mammal species: harbour porpoise (*Phocoena phocoena*), harbour/common seal (*Phoca vitulina*) and grey seal (*Halichoerus grypus*). None of these species are specified in the Irish Sea model, which contains the mammal functional groups: baleen whale, toothed whale and seals. The description of marine mammals in the Irish Sea model was the focus of a model re-structuring by Hernandez-Milian (2014). Following this, the existing Irish Sea mammal groups were removed and five new functional groups were added for specific species: bottlenose dolphin (*Tursiops truncates*), harbour porpoise, minke whale (*Balaenoptera acutorostrata*), common seal and grey seal. Input parameters including biomass, P/B, Q/B and diet for these functional groups were taken from Hernandez-Milian (2014).

At the opposite end of the food web, primary producers, particularly phytoplankton, were key functional groups in the Sellafield model as ^{14}C enters the food web through uptake by primary producers during photosynthesis. Phytoplankton biomass and P/B were re-calculated using the formula from Gowen and Bloomfield (1996) and primary productivity estimates from Gowen *et al*. (2000) of 97 g/m^2 for the coastal Irish Sea. This resulted in an increase in biomass (from 9. 7 to 13.8 t/km^2) and a reduction in the P/B value (from 152.5 to 70.1 $year^{-1}$).

Ecopath also requires diet estimates of each functional group and the diet matrix was largely carried over from the Irish Sea model. Where groups were combined, new diet

estimates were calculated from previous diets as a function of each group's biomass. Where new groups were created, the diet was assumed to be the same; for example, herring and "other small pelagic planktivorous fish" have the same diet. Diets for the new mammal groups were taken from Hernandez-Milian (2014). The diets for two functional groups, small sharks and monkfish (*Lophius piscatorius*), were edited for better definition: small shark and monkfish diet were updated according to Ellis *et al*. (1996) and Crozier *et al*. (1985) respectively. The Sellafield model input parameters and diet matrix are included in the supplementary material (Appendix 3, tables A.5 and A.6).

The Irish Sea model contained nine fisheries which were retained in the Sellafield model. Landings and discards of these fisheries were corrected for the new and combined functional groups but no other changes were made.

6.2.3 PREBAL and balancing

After the described changes to the model were made, model assumptions were tested following a set of pre-balance diagnostics (PREBAL) described by Link (2010). PREBAL checks that the ecosystem model makes ecological and thermodynamic sense by checking the slopes of biomass ratios and other data input against trophic levels. There were no significant issues with the Sellafield model, however, the annual P/B ratios for dab (2.4) and other flatfish (2.2) did appear to be high and conversely, the P/B ratios for herring (0.7) and "other small pelagic planktivorous fish" (0.7) appeared to be relatively low. No changes were made to the input parameters for these groups following PREBAL, however, the groups were highlighted again during model balancing.

The Ecopath model must be mass-balanced after entering the input parameters (Heymans *et al*., 2016). The Sellafield model was initially imbalanced and several parameters were subsequently corrected, as explained below. Increases in biomass for whiting (8.5%), and lobster and large crabs (12.2%), are within the biomass estimates reported by Lees and Mackinson (2007). The biomass increases to the "epifaunal mesobenthos" (0.27%), and "prawn and shrimp" (1.8%), are negligible relative to the changes in biomass made by Lees and Mackinson (2007) when balancing the Irish Sea model. Large differences were found in the Irish Sea model between the initial biomass values used and the balanced biomasses for monkfish, flatfish (small, medium and large), Nephrops and zooplankton groups. Biomasses were estimated in Ecopath for monkfish, dab, other flatfish, Nephrops

and zooplankton by setting ecotrophic efficiency (EE) to 0.95 for these groups. This assumes that the model uses all but 5% of the production of that group and Ecopath can estimate a biomass based on this assumption. In addition, the P/B ratios for dab and other flatfish were estimated in Ecopath by setting the production/consumption (P/Q) ratio for these groups to 0.2. These changes were made based on best practices described by Heymans *et al*. (2016). As herring P/B had been identified as being relatively high, it was re-calculated using fishing mortality (F) from Lees and Mackinson (2007) and natural mortality (M) from FishBase (Froese and Pauly 2016) as P/B is equal to total mortality (Z). Mackerel Q/B was corrected using default values from FishBase including a mean temperature of 10 °C. Corrections were also made to the diet matrix for model balancing and the most significant of these was the reduction in consumption of discards which was relatively high in the Irish Sea model, e.g. the proportion of discards in the diet of Nephrops was reduced from 0.5 to 0.03. This was balanced by increasing the proportion of particulate organic matter in diets. A further important change was a substantial increase in the proportion of polychaetes in dab diet as described by (Gibson and Ezzi 1987). All changes made to both the input parameters and the diet matrix for model balancing are shown in Appendix 3, tables A.5 and A.6.

6.2.4 Ecospace

To accurately predict uptake of Sellafield ^{14}C in the marine environment, the Sellafield model had to be spatially resolved. In Ecospace, the biomass (B) of a functional group for a specific grid-cell at time t can be expressed as:

$$\frac{dB}{dt} = (I + g.C) - (Z + E).B$$

where I is the total immigration rate from surrounding cells, g is the net growth efficiency, C is food consumption rate, Z is total instantaneous mortality rate, and E is total instantaneous emigration rate (Walters *et al*., 1999).

Due to the net northward dispersion of ^{14}C and the available data for the West of Scotland (Tierney *et al*., 2017a, 2017b) the Ecospace base-map (Figure 6.1) of the Sellafield model, produced in ArcGIS, encompasses part of the West of Scotland marine environment as well as the Irish Sea. Base-map grid resolution was 5 km^2 with boundaries at approximately 56° 45’ N (northern boundary), 02° 45’ W (eastern boundary), 53° 15’ N (southern boundary) and 7° 15’ W (western boundary). The base-map covers key sites in both

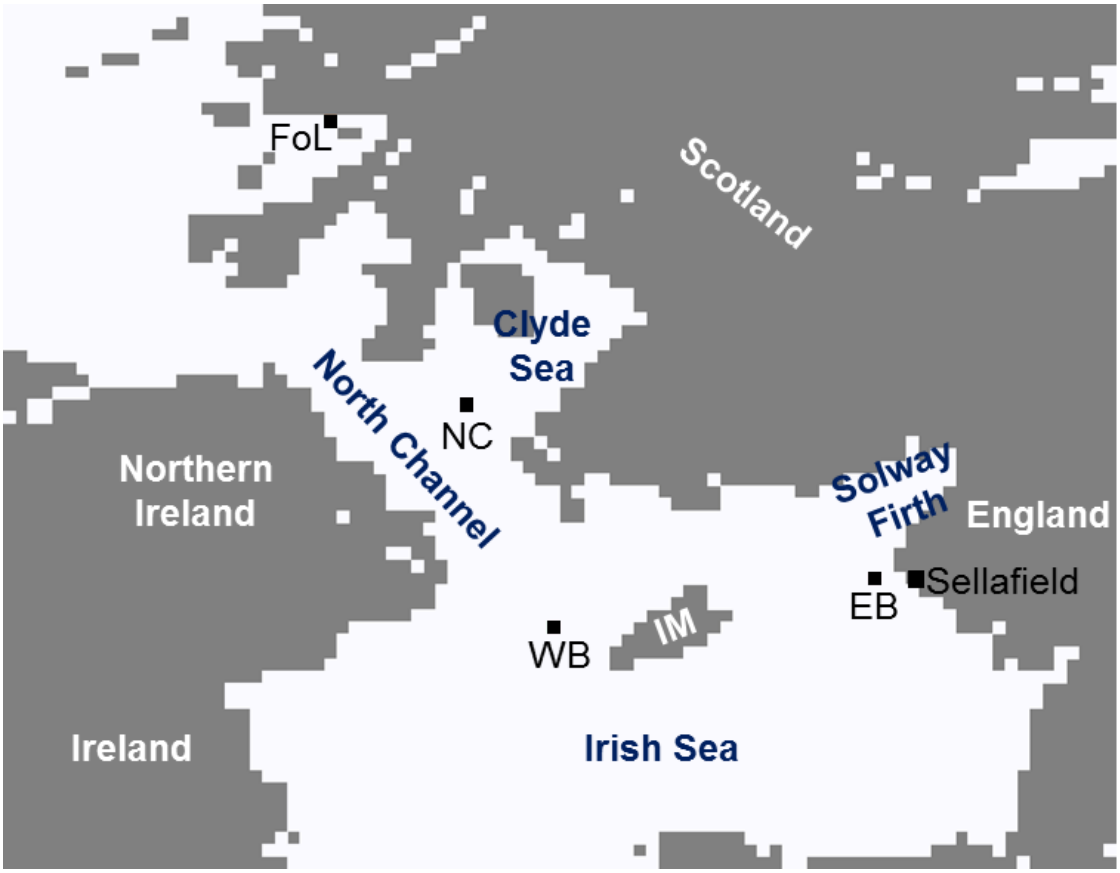

Figure 6.1. Annotated Sellafield model Ecospace base-map with 5 km^2 resolution (IM = Isle of Man). Grid cells representing sample stations (EB, WB, NC and FoL) from Muir *et al*. (2017) and Tierney *et al*. (2017a) are also shown.

the Irish Sea and West of Scotland, used in studies concerning ^{14}C in the environment (Muir *et al*., 2017; Tierney *et al*., 2017a, 2017b).

The contaminant map layer in Ecospace allows the user to input contaminant concentrations across the base-map. This can also be used to select a specific point source for a contaminant which is limited to the base-map resolution. A contaminant can be dispersed in Ecospace using the base dispersal rate for the first detrital group listed in the model. The base dispersal rate is used to set the rate organisms in the ecosystem will disperse due to random movements where the default is 300 km year^{-1} but this can also be applied to a contaminant. In addition, a more realistic dispersion pattern can be created using the advection map layer by inputting x and y velocity data at the base-map resolution. Ecospace advection would typically be fixed for the duration of the model run, however, by using the spatial-temporal framework (Steenbeek *et al*., 2013) the velocities were varied through time. Month averaged x and y velocities at 8 km^2 resolution from a hind-cast model of the north-east Atlantic, for the period January 1985 to June 2014 (most recent data available at the time of study), were sourced from the European Commission Copernicus Marine Environment Monitoring Service (http://marine.copernicus.eu). Data for the model area were extracted and velocities were depth averaged. The data were extrapolated over the base-map 5 km^2 resolution and a time-series of map files (ASCII) for x and y velocities on monthly time steps were produced. These data files were read into Ecospace using the spatial-temporal framework (Steenbeek *et al*., 2013) to create advection fields and the model was run on monthly time-steps. Phytoplankton and zooplankton dispersion, as well as contaminant dispersion, were linked to model advection.

.2.5 Ecotracer

The iteration of EwE used for the Sellafield model contained changes to the Ecotracer component not implemented in the most recent downloadable version (EwE 6.5). When running Ecotracer in Ecosim (non-spatial contaminant modelling) it is possible to link contaminant inputs to a data time-series. To do this for a point source in Ecospace, a new Ecotracer function was added which allows variable contaminant input at specified grid cells, limited to the base-map resolution. For the Sellafield model, this means that ^{14}C input was in a 5 km^2 area, offshore from Sellafield, where the pipelines end. This input was made as total monthly ^{14}C discharge activity from Sellafield in Becquerels (Bq).

Other input parameters in Ecotracer include: initial contaminant concentration, contaminant concentration in immigrating biomass, direct uptake, physical decay rate, proportion of contaminant excreted and metabolic decay rate (Walters and Christensen, 2017). The input values used are shown in Table 6.1. Initial contaminant concentrations must be set for both the environment and the functional groups. Sellafield ^{14}C discharges are in addition to an existing "background" ^{14}C activity from natural production and atmospheric atomic weapons testing. The initial contaminant concentration in the Sellafield model was set at zero and, as the only input was from Sellafield ^{14}C discharges, any increase in functional group contaminant concentration shows net ^{14}C enrichment in excess of background.

Direct uptake is the rate at which a functional group takes up the contaminant from the environment. ^{14}C is discharged to the marine environment as DIC and primary producing organisms incorporate dissolved inorganic ^{14}C, through fixation of carbon during photosynthesis into soft tissue. For phytoplankton, direct uptake was calculated as the rate at which phytoplankton photosynthesise as it is assumed that ^{14}C uptake is identical to stable carbon uptake. Following Walters and Christensen (2017) this is expressed as:

$$Direct\ uptake = u_i/B_i/C_0$$

where u_i is the mass of carbon intake by primary producer i, B_i is the biomass of primary producer i and C_0 is the DIC concentration. Phytoplankton ^{14}C uptake was calculated using the primary productivity estimate of 97 g m^{-2} for the coastal Irish Sea (Gowan *et al*., 2000), the calculated biomass 124.5 t km^{-2} and an estimated DIC concentration of 30 mg l^{-1}, taken from the upper limit of typical DIC concentrations in seawater of 24-30 mg C l^{-1} (Chester, 1990). Primary productivity rates for the other primary producers, seaweed and microflora were estimated by back calculating from the model biomass using formula from Gowen & Bloomfield (1996). Productivity rates of 450 g m^{-2} (seaweed) and 230 g m^{-2} (microflora) were then used to calculate direct uptake for these groups. Contaminant uptake for consumer groups is a function of the contaminant concentration in their diet, their consumption rate and their mortality (Walters and Christensen 2017).

Table 6.1. Sellafield model Ecotracer parameters.

Group Name	Initial Conc. (t/t)	Direct uptake rate (t/t/t/year)	Proportion excreted	Metabolic decay rate (/year)
Bottlenose Dolphin	0	0	0.2	6.836
Harbour Porpoise	0	0	0.2	6.836
Minke Whale	0	0	0.2	7.980
Common Seal	0	0	0.2	11.520
Grey Seal	0	0	0.2	11.520
Seabirds	0	0	0.2	65.056
Large Sharks	0	0	0.2	2.226
Small Sharks	0	0	0.2	6.804
Basking Sharks	0	0	0.2	2.890
Skates and Rays	0	0	0.2	11.200
Cod	0	0	0.2	2.375
Haddock	0	0	0.2	4.353
Plaice	0	0	0.2	3.146
Whiting	0	0	0.2	1.534
Sole	0	0	0.2	1.201
Monkfish	0	0	0.2	1.193
Dab	0	0	0.2	1.825
Other Flatfish	0	0	0.2	2.314
Dragonets	0	0	0.2	2.583
Mackerel	0	0	0.2	3.106
Ling	0	0	0.2	1.156
Other Demersals	0	0	0.2	2.133
Herring	0	0	0.2	4.059
Other Planktivorous Fish	0	0	0.2	4.486
Sandeels	0	0	0.2	2.483
Epifaunal Macrobenthos	0	0	0.2	4.983
Epifaunal Mesobenthos	0	0	0.2	5.436
Infaunal Macrobenthos	0	0	0.2	8.085
Infaunal Mesobenthos	0	0	0.2	6.728
Infauna (Polychaete)	0	0	0.2	6.138
Lobster and Large Crabs	0	0	0.2	3.393
Nephrops	0	0	0.2	3.164
Cephalopods	0	0	0.2	10.019
Prawns and Shrimp	0	0	0.2	4.155
Sessile Epifauna	0	0	0.2	6.198
Meiofauna	0	0	0.2	30.750
Zooplankton	0	0	0.2	25.476
Seaweed	0	0.002	0	6.000
Microflora	0	0.020	0	58.700
Phytoplankton	0	0.002	0	7.014
Particulate Organic Matter	0	0	0	n/a
Dissolved Organic Matter	0	0	0	n/a
Discards	0	0	0	n/a

There are two excretion parameters for each functional group. The proportion of contaminant excreted is the proportion not assimilated into the biomass and so passes straight into the detritus group. The default annual unassimilated consumption for consumer groups in the Ecopath parameters is 0.2 and this was copied for the proportion of contaminant excreted in the Sellafield model as ^{14}C acts as a tracer of stable carbon and, therefore, energy transfer in an ecosystem. The metabolic decay rate is the rate at which assimilated contaminant is released back into the environment (see "excretion" in Walters and Christensen, 2017). The carbon weight ^{14}C activity (Bq per mass C) of marine primary producers is in equilibrium with the DIC ^{14}C activity. Therefore, the metabolic decay rate for primary producers can be calculated where the equilibrium ratio of ^{14}C in a primary producer is equal to the environmental concentration. For example, when the DIC ^{14}C activity is at background (approximately 249 Bq kg^{-1} C), the ^{14}C activity in a primary producer is expected to be the same. Under these conditions the metabolic decay rate can be expressed as:

$$Metabolic\ decay\ rate = D_i . C_0 / \left(\frac{C_i}{B_i}\right)$$

where D_i is the direct uptake rate for the primary producer i, C_0 is the ^{14}C concentration in the environment, C_i is the ^{14}C concentration in primary producer i and B_i is the biomass of primary producer i. The metabolic decay rate was calculated this way for all three primary producers in the Sellafield model. For consumer groups, the metabolic decay rate was assumed to be equal to the respiration rate / biomass which were calculated in the Ecopath component during model balancing.

A contaminant physical decay rate parameter was added to the Ecotracer module in the version used here. This can be set for both the environment and each functional group. For radionuclides, this is the physical radioactive decay rate, meaning that in EwE, biological decay and physical radioactive decay are two separate parameters. ^{14}C has a long half-life of 5730 years and the impact of radioactive decay on a model running over several decades is negligible, and so, physical decay rate was set at zero. As the Ecopath food web model contained no immigration, the contaminant concentration in the immigrating biomass could also be set to zero for every functional group.

Muir *et al*. (2017) and Tierney *et al*. (2017a) describe ^{14}C activities at numerous sites including 4 main stations (Figure 6.1) located in the Irish Sea east basin (EB), Irish Sea west basin (WB), North Channel (NC) and Firth of Lorn (FoL). Model base-map grid cells

at these site locations or, in the case of FoL, as close as possible, were labelled as different model regions in Ecospace and data specific to these regions were extracted from EwE. Model data analyses were conducted and map figures were produced using R (R Development Core Team 2017) and the R package "ggmap" (Kahle and Wickham 2013) used to overlay model predicted data over Google satellite maps. Model predictions are only given where ^{14}C enrichment is at least 1 Bq kg^{-1} C and all observed ^{14}C activities are given as net activities (i.e. background subtracted).

6.3 Results and Discussion

6.3.1 ^{14}C Dispersion

Although advection was the dominant control on the general direction and extent of model ^{14}C dispersion, contaminant base dispersal rate had a significant impact (Figure 6.2). As ^{14}C uptake by primary producers is limited to the ^{14}C activity of the environment (or DIC ^{14}C activity) for a given cell, the physical dispersion of Sellafield ^{14}C is a key mechanism. Studies examining the dispersion of other highly soluble radionuclides discharged by Sellafield (e.g. ^{134}Cs, ^{137}Cs and ^{99}Tc) have estimated transit times from Sellafield to the North Channel of between 3 months and 1.8 years (Jefferies *et al*., 1973, Kershaw and Baxter 1995, Kershaw *et al*., 2004). Similarly, transit times of between 3 months and 1 year were predicted by the model developed by Dabrowski and Hartnett (2008). Using a base dispersal rate of at least 100 km per month resulted in model ^{14}C reaching the North Channel within 1 year (Figure 6.2). As the distance between Sellafield and the North Channel is approximately 110 km, it is apparent that model dispersion of ^{14}C is limited by both advection and uptake by primary producers. Increasing the base dispersal rate does increase maximum dispersal extent, though this increase does not appear to be substantial. It does reduce the maximum DIC ^{14}C activities predicted in pockets where ^{14}C appears to accumulate, e.g. the Solway Firth. This accumulation, particularly at lower base dispersal rates, causes activities to increase to levels which have not been observed in previous studies. For example, the model predicted ^{14}C activities above 30 KBq kg^{-1} C between 2001 and 2006 when using a base dispersal rate of 100 km per month. However, an increase in base dispersal rate to 200 km per month, limited maximum model DIC activities to less than 20 KBq kg^{-1} C. There are no reported DIC ^{14}C activities for the period of peak predicted activity (2001-2006) and, therefore, no available data for DIC activities in areas such as the Solway Firth where a significant accumulation of ^{14}C was predicted for this

period. The highest reported net DIC ^{14}C activities are approximately 8550 Bq kg^{-1} C in 1995 (Cook *et al*., 1998) and 4500 Bq kg^{-1} C in 1997 (Cook *et al*., 2004), at sites relatively close to Sellafield. Using a time-series of DIC ^{14}C activities for a site in the vicinity of Sellafield for the period 1989 to 1999 (Cook *et al*., 2004), it is shown that the range of activities predicted by the model when using a base dispersal rate of 200 km per month was similar to the observed range through time (Figure 6.3). Although the specific measured and predicted activities do not generally align, it is important to recognise that model ^{14}C activities are predicted per km^2 (for a 5 km^2 cell) per month, whereas measured DIC samples were taken from a specific day and location on the coastline. Model dispersion of DIC ^{14}C could be improved with further measurements at sites such as the Solway Firth to address uncertainty in dispersion. To illustrate model dispersion of dissolved inorganic ^{14}C in the environment a video component (Video 1) is available and accompanies the electronic version of the manuscript (see video stills in Figure 6.2 in thesis version).

In addition to the Solway Firth, accumulation of ^{14}C occurs in the south-east Irish Sea and around the Isle of Man. Circulation models have described a significant seasonal southward flow in the Irish Sea (Dabrowski and Hartnett 2008; Dabrowski *et al*., 2010) creating a backwater in the south-east Irish Sea. This could result in the area around Liverpool Bay being a significant sink for radionuclides released from Sellafield (Dabrowski and Hartnett 2008). An increase in the radionuclide inventories of saltmarsh sediments in areas including the Solway Firth has previously been suggested (MacKenzie *et al*., 1994). However, an accumulation of Sellafield radionuclides in the water column of the Solway Firth and also around the Isle of Man has not been previously detected and the general northward movement of water continuously flushed the Isle of Man coastline in circulation models (Dabrowski and Hartnett 2008). Although accumulation of ^{14}C in these areas could occur, any accumulation in concentration may not occur to the same extent predicted by the EwE model. Greater retention of ^{14}C at these sites will result in reduced dispersion to more distant areas. The fact that modelled ^{14}C dispersion does not significantly penetrate the Scottish west coast, suggests that model retention in the Irish Sea is too high. Previous studies have shown that a significant proportion of Sellafield discharges are dispersed around the Scottish coastline (Gulliver *et al*., 2001; Tierney *et al*., 2016, 2017a). The consequence of using depth averaged advection in our study is that the necessary complex hydrodynamics to drive dispersion at this regional scale may not be well addressed in this model. At coastal areas, such as the Solway Firth, dispersion will be

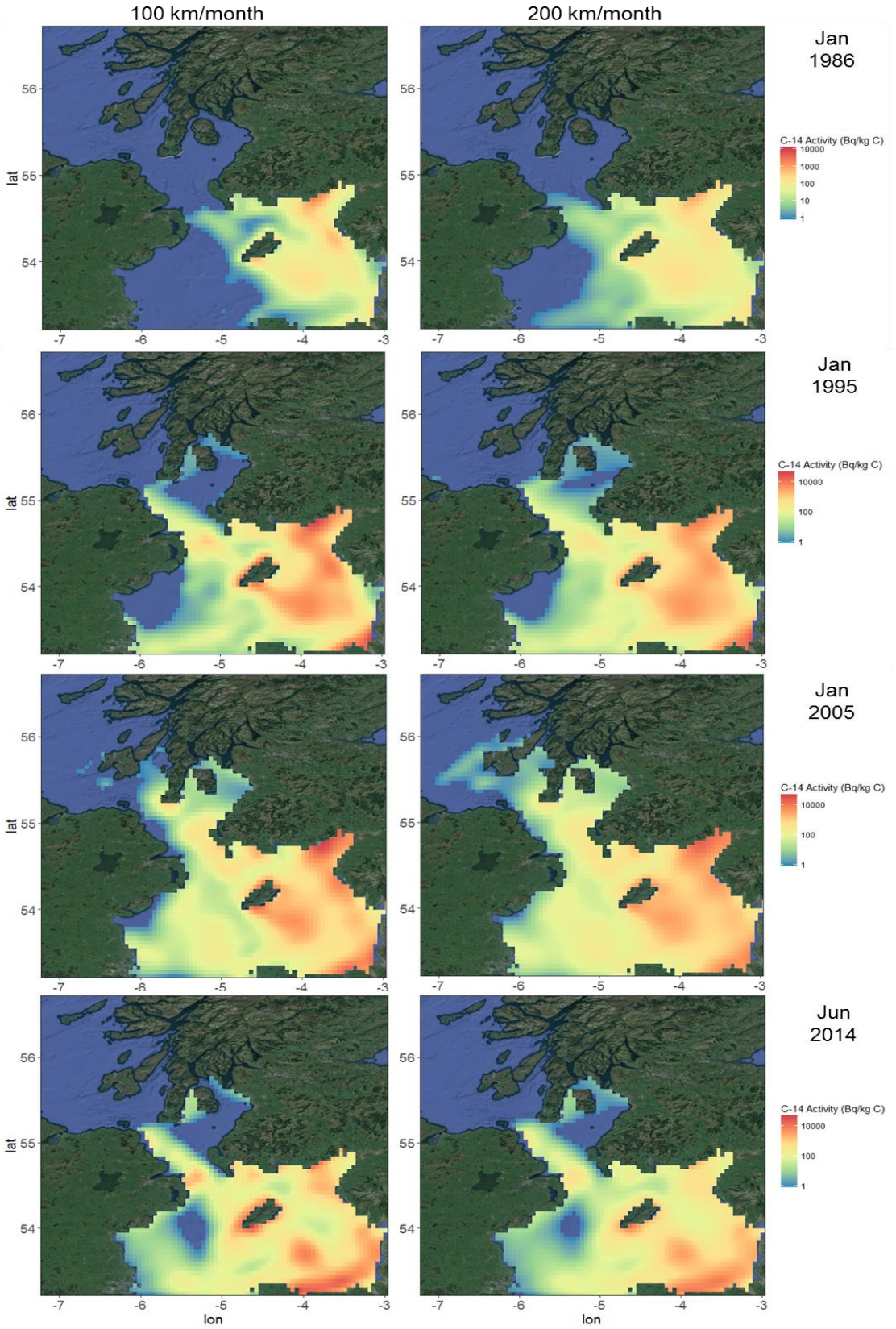

Figure 6.2. Modelled DIC ^{14}C activities (calculated from modelled environmental ^{14}C activity) for four different months using two different base dispersion rates: 100 km per month (left) and 200 km per month (right). Note that the ^{14}C activity scale increases to 40 KBq kg^{-1} C from January 1995 to account for higher predicted activities particularly at the lower dispersion rate.

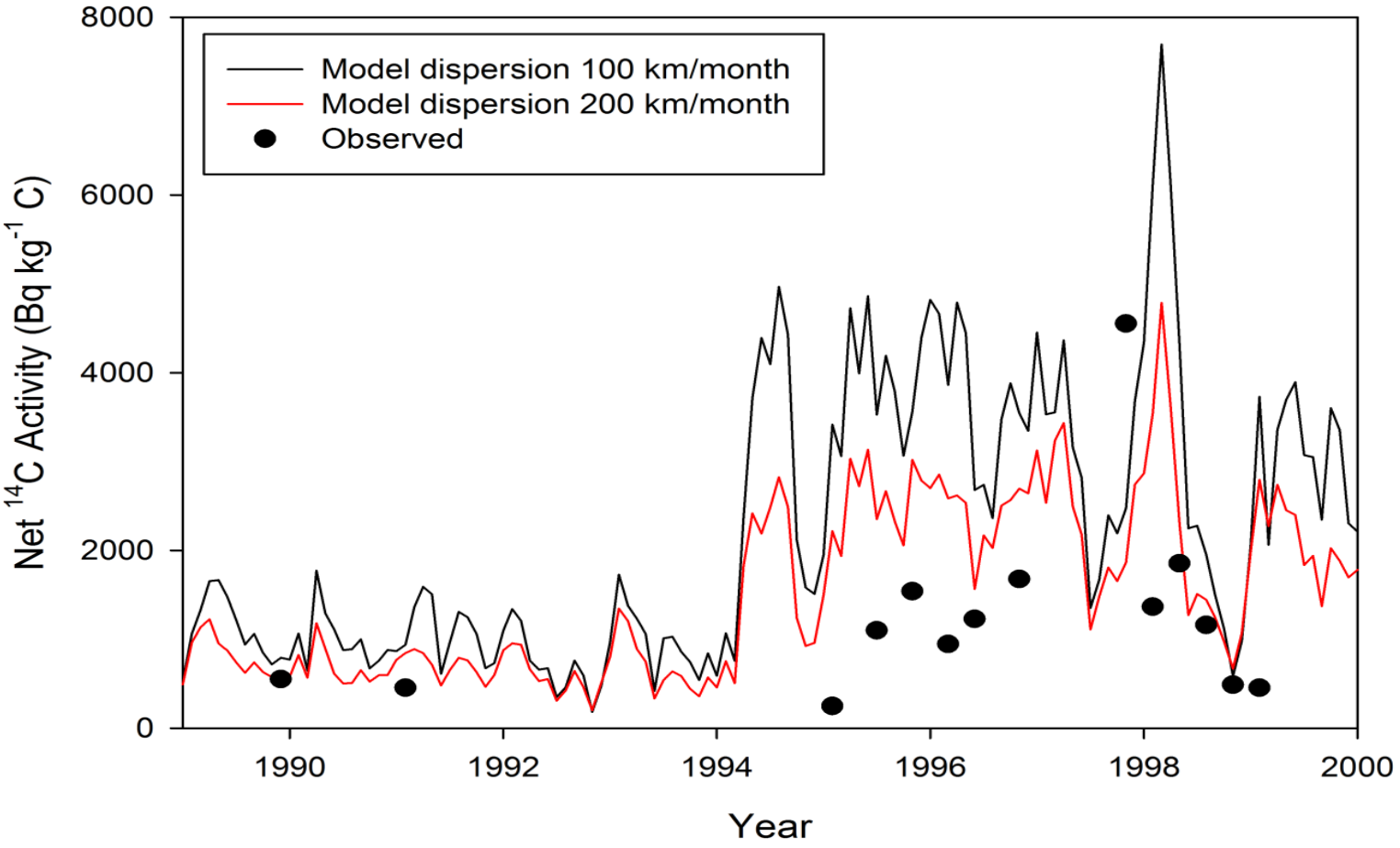

Figure 6.3. Modelled DIC ^{14}C activities between 1989 and 2000 from offshore Sellafield compared to activities observed in Cook *et al*. (2004).

complicated by freshwater input and non-uniform current direction at different depths which would reduce the overall retention of dissolved ^{14}C at these sites. Using depth averaged advection means that dissolved ^{14}C can be trapped and accumulate exponentially at sites if advection is directed towards the coastline, although this is significantly reduced by increasing the base dispersal rate. Dispersion is also limited by data and map resolution. The velocity data used had a resolution of 8 km^2 so any local physical dynamics were lost. The 5 km^2 base-map resolution meant that many features of the UK coastline were not well defined, including the loss of several islands on the Scottish west coast that are connected to the mainland in the model.

6.3.2 ^{14}C Ecological Fate

Muir *et al*. (2017) reported ^{14}C activities for DIC and a number of species at sites in the Irish Sea east basin (station EB) and west basin (station WB) in June 2014. Model ^{14}C activities at EB in June 2014 were significantly over-predicted compared to observed activities when using a low dispersal rate (100 km per month) but a higher base dispersal rate (200 km per month) brought the predicted and observed activities significantly closer (Figure 6.4). Trends in the observed data were replicated by the model. Phytoplankton and zooplankton ^{14}C activities were relatively low compared to benthic species and dab ^{14}C activity was the highest; although a large range in observed dab activity (499-763 Bq kg^{-1} C) meant that the average dab activity (631 Bq kg^{-1} C) was less than the infaunal macrobenthos (704 Bq kg^{-1} C). The model did not capture this high infaunal macrobenthos ^{14}C activity relative to most other groups. The observed infaunal macrobenthos activity comes from green spoon worm (*Maxmuelleria lankesteri*) tissue and this species is known to have an important role in the redistribution of other Sellafield-derived radionuclides in bottom sediments (Hughes *et al*., 1996; Kershaw *et al*., 1983, 1984, 1999). Its inclusion as a separate species in the model was considered, however, this was deemed to be challenging due to limited ecological data.

Station WB is more complex due to highly variable reported ^{14}C activities between species (Muir *et al*., 2017). Typically, both high and low dispersion rates under-predicted the observed higher activities (in polychaetes, epifaunal macrobenthos and dab) and over-predicted the observed lower activities (e.g. phytoplankton and zooplankton; Figure 6.5). However, the main observed trends were again predicted. As for EB, plankton ^{14}C activities were significantly lower than other functional groups and dab activity was again

predicted to be the highest. The relatively high ^{14}C activity observed in polychaetes (405 Bq kg^{-1} C) was due to the higher observed net activity of the predatory species *Aphrodita aculeate* (740 Bq kg^{-1} C) whereas the average activity of other polychaete species was lower (69 Bq kg^{-1} C) and similar to the model predicted activity of 59 Bq kg^{-1} C. The observed epifaunal macrobenthos activity was also relatively high (488 Bq kg^{-1} C) and not captured by the model. Similar to the polychaete group, the model functional group epifaunal macrobenthos was made up of numerous species and the observed ^{14}C activity was comprised from an average of starfish species only and may not accurately represent the entire functional group. Both these cases indicate that model functional groups were not well defined in some instances, as, for example, the addition of a predatory species to a functional group is not best practice (Heymans *et al*., 2016).

A number of ^{14}C activities, across a range of species, were reported by Tierney *et al*. (2017a) for two sites in the West of Scotland marine environment; the North Channel (station NC) and Firth of Lorn (station FoL). Due to northward dispersion of ^{14}C being constrained in the model, as a result of Irish Sea retention of ^{14}C being too high, the model under-predicts activities at these sites relative to the observed activities. Additionally, the connection of several islands to the Scottish mainland, due to the 5 km^2 base map resolution, blocked important channels in the West of Scotland area including to the south of the Firth of Lorn (preventing direct northward dispersion of ^{14}C to this area) and much of the Firth of Lorn itself. The lack of penetrative northward dispersion of ^{14}C resulted in the model showing no ^{14}C enrichment at FoL in 2014, although a small enrichment in DIC and benthic species was observed (Tierney *et al*., 2017a). The model only predicted a slight enrichment (1-2 Bq kg^{-1} C) in DIC and some functional groups at FoL between 2005 and 2009. At station NC, the observed trend of low plankton activities and higher benthic activities was again replicated in June 2014 (Figure 6.6). As observed, whiting activity was predicted to be higher than other groups and repeated the theme where the group with the highest modelled trophic level also had the highest activity (see dab for Irish Sea sites). However, the comparatively high activity observed in whiting at the NC station was interpreted as being likely due to northward migration of whiting which had foraged in the Irish Sea (Tierney *et al*., 2017a).

The issues discussed with the model ^{14}C dispersion meant that predicted activities for harbour porpoises did not typically align with the activities reported by Tierney *et al*. (2017b). It should also be noted that although harbour porpoise is a resident species, and

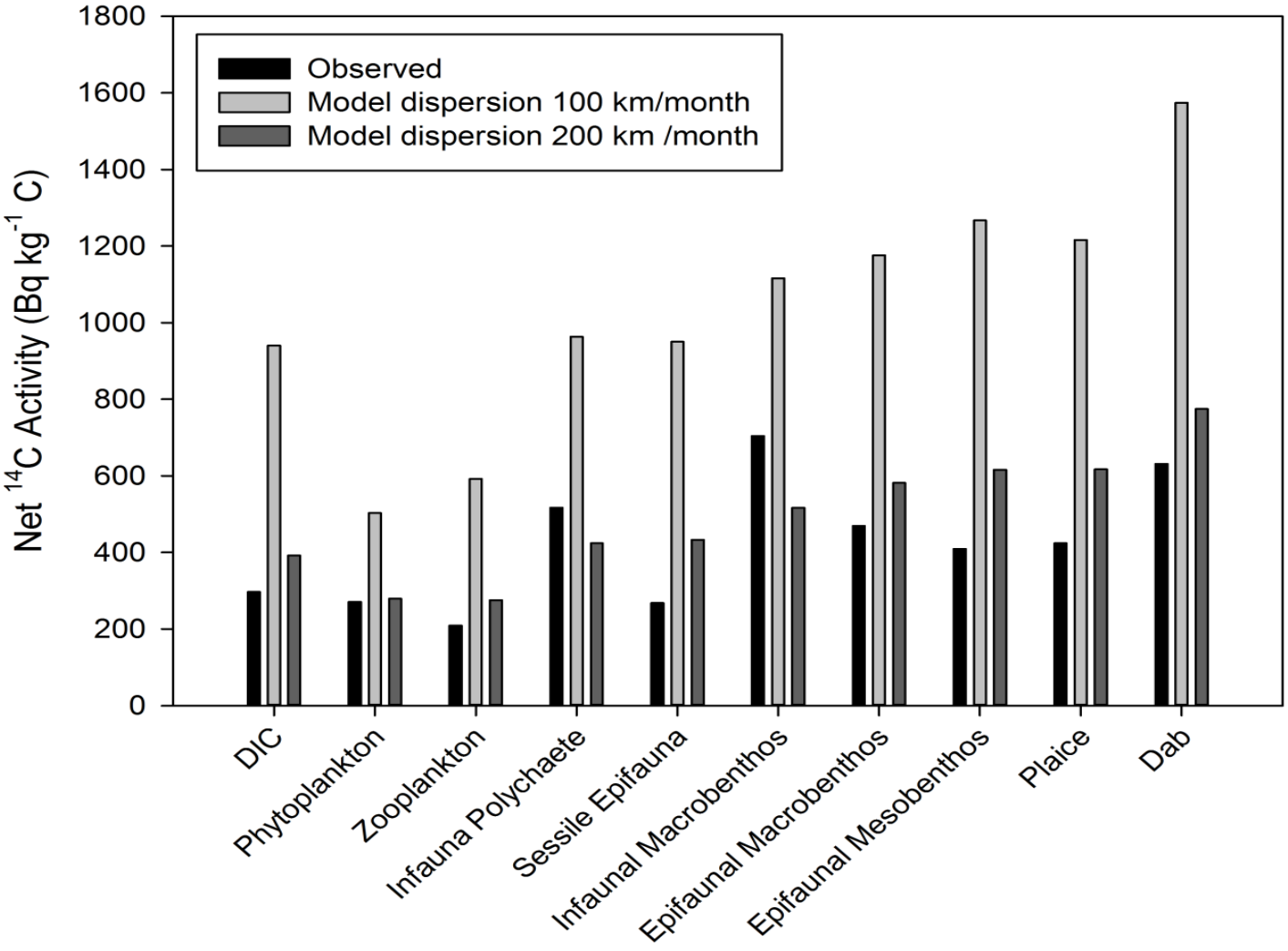

Figure 6.4. Modelled DIC and selected functional group ^{14}C activities for June 2014 at station EB compared to activities observed in Muir *et al*. (2017).

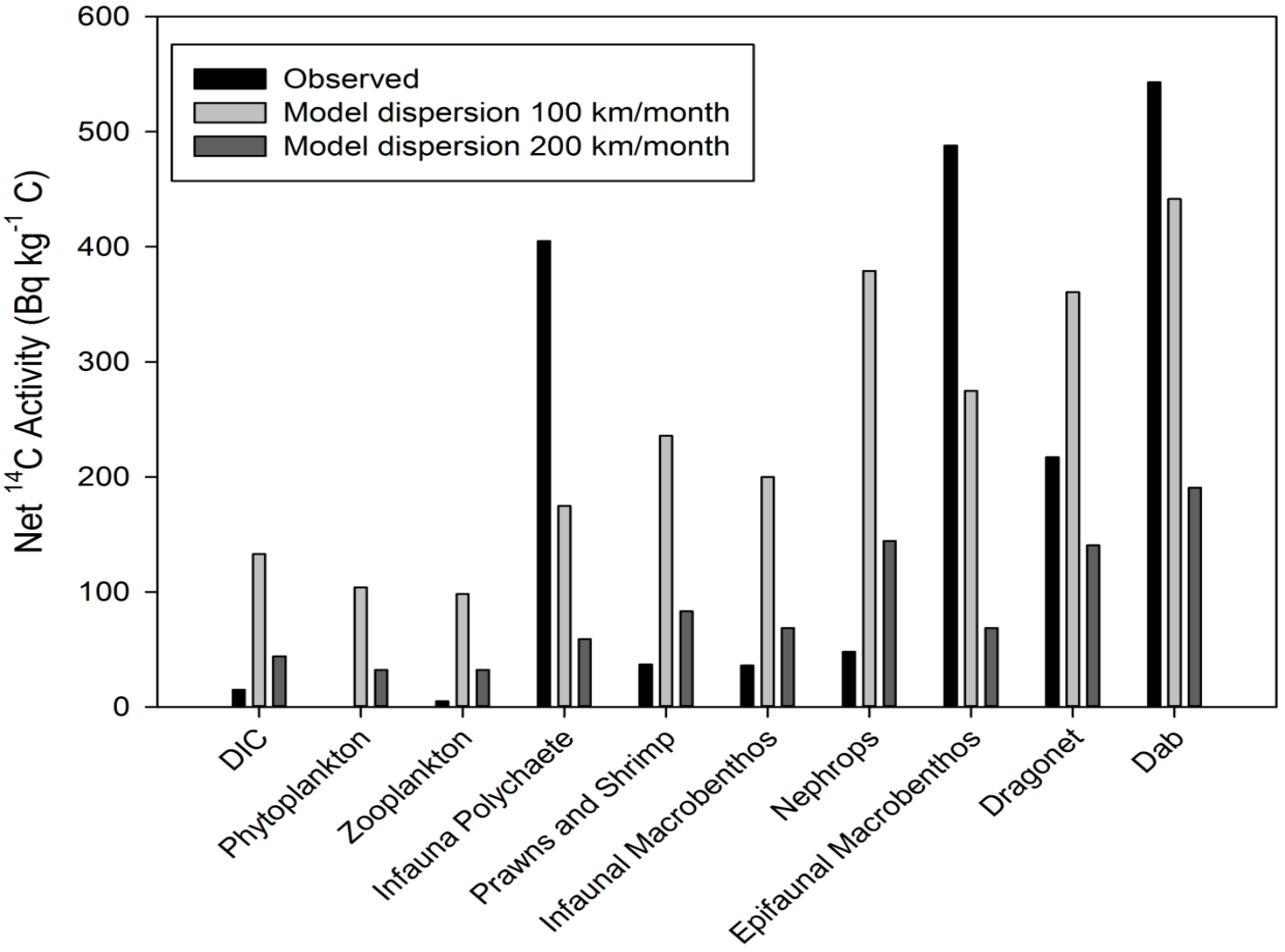

Figure 6.5. Modelled DIC and selected functional group ^{14}C activities for June 2014 at station WB compared to activities observed in Muir *et al*. (2017).

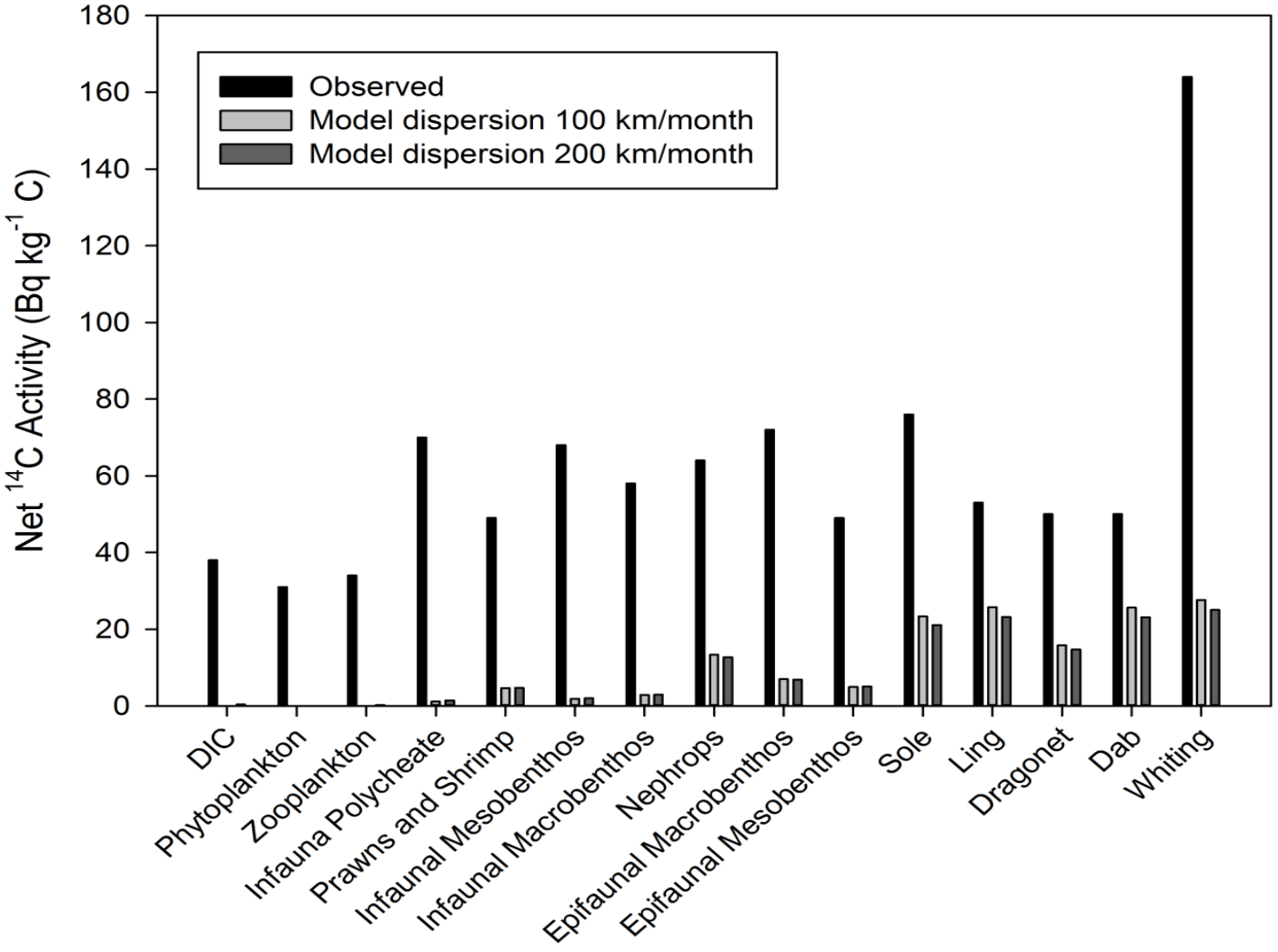

Figure 6.6. Modelled DIC and functional group ^{14}C activities for June 2014 at Station NC compared to activities observed in Tierney *et al*. (2017a).

observed ^{14}C activities indicate a high feeding fidelity (Tierney *et al*., 2017b), these are animals that can traverse the modelled area and single measurements from a stranded individual is unlikely to represent the average activity across the population in that area. Predicted trends through time do, however, appear to replicate the observed trends as illustrated by comparing predicted harbour porpoise ^{14}C activities in four different years (1993, 2002, 2004 and 2014) with the observed activities for those years (Figure 6.7). Both predicted and observed ^{14}C activities show very low ^{14}C activities of between 0 and 10 Bq kg^{-1} for West of Scotland porpoises north of the North Channel in 1993, with activities significantly higher in the south-east Irish Sea. Peak discharges between 2001 and 2005 increased porpoise ^{14}C activity in the north-east Irish Sea and activities were lower in the North Channel and Clyde Sea. Clyde Sea ^{14}C activities were lower in 2014 but activities in the North Channel remained relatively higher and the highest activities were found in the south-east Irish Sea.

The Sellafield model illustrates that ecosystem uptake of ^{14}C for a specific area is controlled by the DIC ^{14}C activity in that area and, therefore, the dispersion of changeable Sellafield ^{14}C discharges through time (Figure 6.8). Phytoplankton and, subsequently, zooplankton ^{14}C activities closely mirror changes in the DIC ^{14}C activity. As ^{14}C transfers to higher trophic levels are not immediate, there is a delayed response to ^{14}C activities which has a smoothing effect on predicted activities through time. Modelled ^{14}C activities for stations EB, WB and NC in June 2014 show a general trend of increasing activity with increasing trophic level (Figures 6.4, 6.5 and 6.6). This is not due to bioaccumulation but rather the lag effect in ^{14}C transfer to higher trophic levels, culminating in top predators such as harbour porpoise. The very low ^{14}C discharge activity in June 2014 caused DIC and plankton activities to drop at station EB whilst other functional group activities remained higher due to uptake of previously higher activities. Variable dispersion of ^{14}C to station WB resulted in DIC and plankton activities decreasing significantly below the ^{14}C activities of other species in June 2014. After a peak in DIC activity at station NC in 2007, the activities at higher trophic levels gradually declined, but not to below the significantly reduced plankton activities. This mechanism, which likely caused the higher observed ^{14}C activities in benthic species, was suggested by Muir *et al*. (2017) and Tierney *et al*. (2017a) who described an integrated ^{14}C activity in older living organisms occupying higher trophic levels. It was also identified through analysis of marine mammal ^{14}C activities alone (Tierney *et al*., 2017b) where mammal ^{14}C activities correlated significantly with Sellafield discharges for the 24 months prior to stranding.

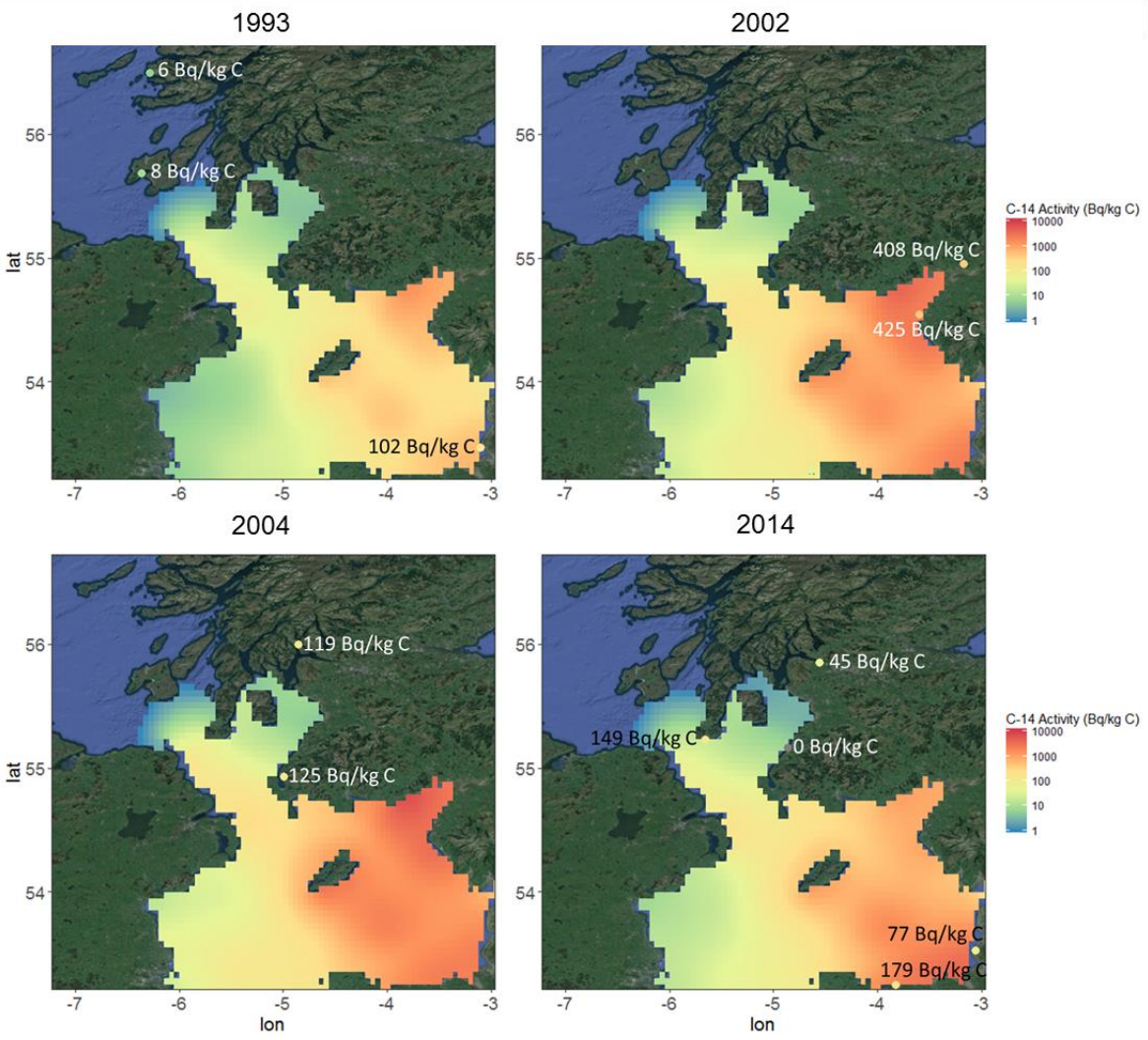

Figure 6.7. Averaged modelled harbour porpoise ^{14}C activities from 1993, 2002, 2004 and 2014 compared to measured activities observed in Tierney *et al*. (2017b) shown as dots with annotated activity.

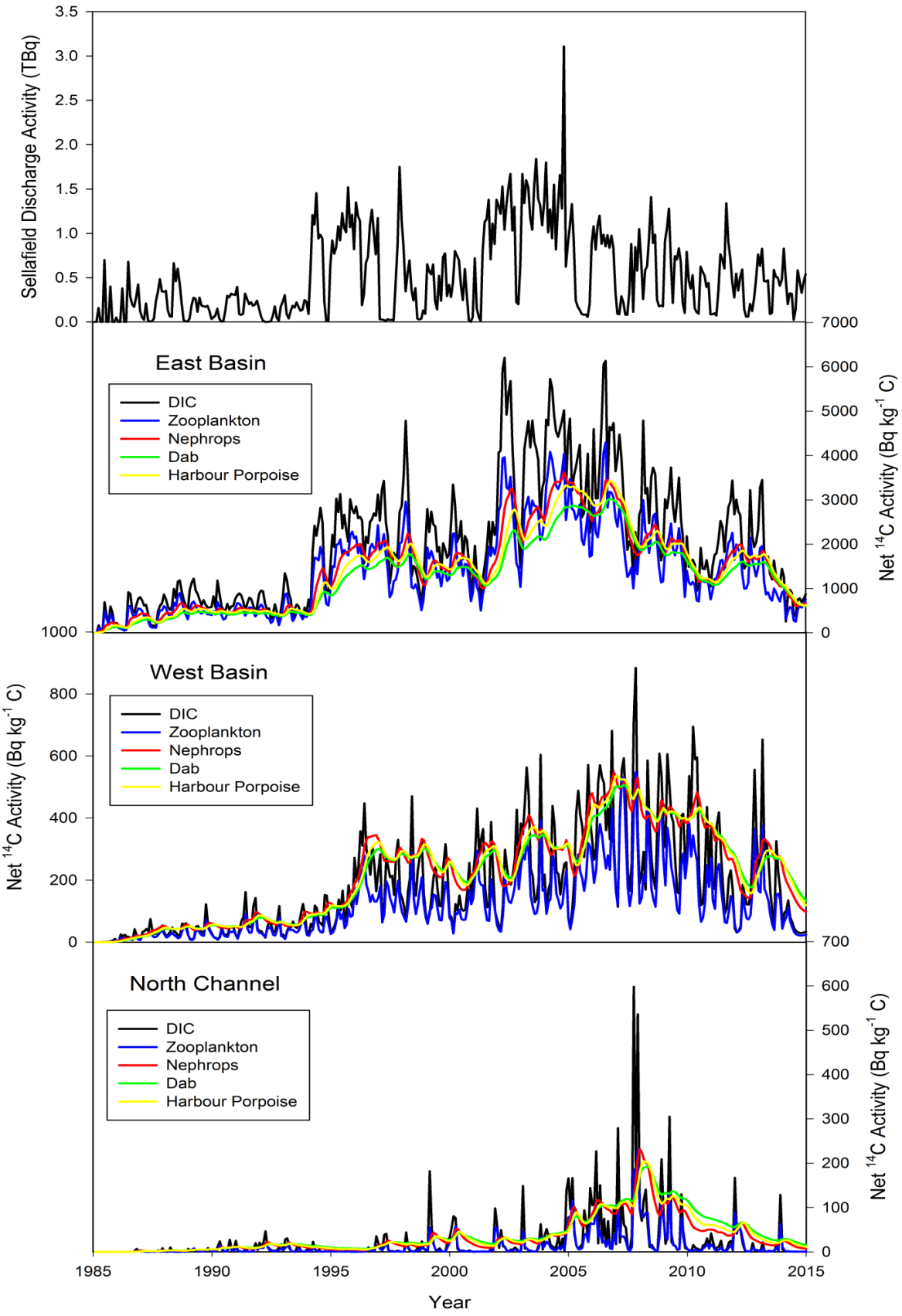

Figure 6.8. Monthly Sellafield ^{14}C discharge data input to the model (top). Modelled DIC and selected functional group ^{14}C activities at the east basin (EB), west basin (WB) and North Channel (NC) stations for the duration of the model run using a high base dispersion rate (200 km per month).

As shown by model results, this means that the ^{14}C activity of an organism is not only dependent on the discharge activity and the dispersion of ^{14}C, which can be highly variable, but is also dependent on the trophic level that the organism feeds at. Feeding at lower trophic levels will result in a species having a highly variable ^{14}C activity through time. Species that feed at higher trophic levels will have ^{14}C activities that are not dependent on the immediate environmental activity and could be significantly more or less enriched in ^{14}C relative to the environment they inhabit. To illustrate the differences in ^{14}C activities spatially and temporally at different trophic levels, a video component (Video 2) is available and accompanies the electronic version of the manuscript (see video stills in Figure 6.9 in thesis version).

6.3.3 Limitations and Advantages

Modelling ^{14}C dispersion within the EwE framework significantly reduces far-field dispersion beyond the Irish Sea in comparison to observed data, and appears to result from increased retention of ^{14}C at specific areas within the Irish Sea. As this study aimed to model the general patterns of ^{14}C dispersion, the velocity and base-map resolutions are appropriate, nevertheless, using depth averaged advection over simplifies the localised oceanographic conditions. In future work, this could be overcome by using a 3-dimensional physical-transport model to disperse ^{14}C in the environment. By using the same approach to which velocity data were input to Ecospace in this study, employing the spatial-temporal framework (Steenbeek *et al.*, 2015), depth-averaged ^{14}C activity/concentration fields predicted by the physical-transport model could be applied instead.

As discussed, the EwE approach accurately demonstrates a number of the observed trends in ^{14}C activities and reproduces the observed transfer of ^{14}C through the marine food-web, after initial uptake by primary producers relative to the environmental ^{14}C activity. It can, therefore, provide a tool which is capable of predicting the ecological uptake of radioactive contamination, or other environmental contaminants (i.e. trace metals), if the environmental concentrations were accurately provided. Predicted activities for a specific functional group are limited by how well each functional group and their ecology are defined in the model. Diet is a key factor in an organisms ^{14}C activity, and diet description data should be revisited and improved (where possible) for the Sellafield model. A major advantage of EwE is that it can predict general trends for contaminant concentrations

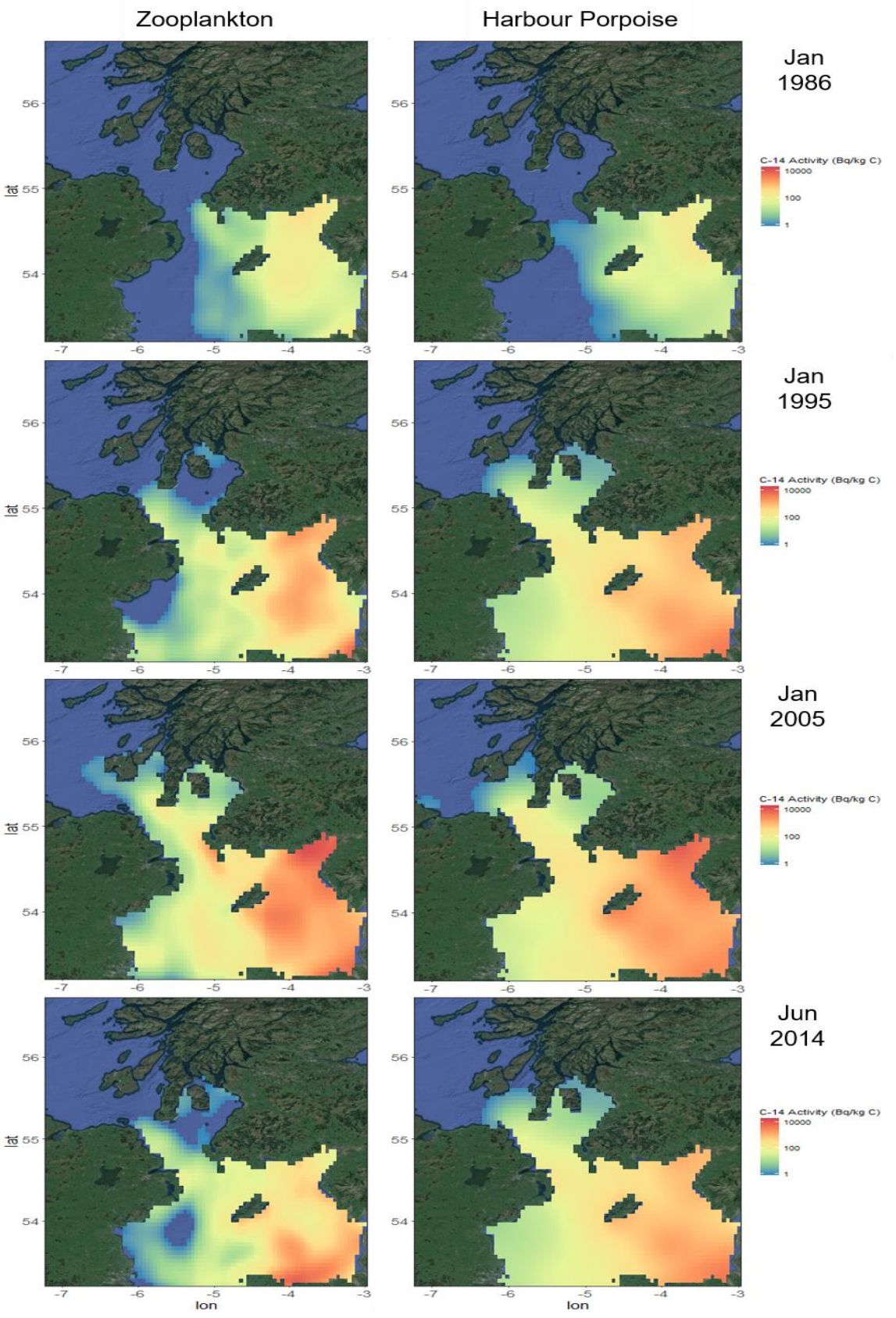

Figure 6.9. Modelled zooplankton and harbour porpoise ^{14}C activities for four different months. Increased variability, both spatially and temporally, in zooplankton ^{14}C activities can be observed relative to harbour porpoise activities which vary more gradually as a result of time-integration of ^{14}C.

in non-specific functional groups, or specific contaminant concentrations in individual species. For example, if the aim was to determine the transfer of ^{14}C or other radionuclides between different benthic species and the sediment, then the functional groups describing these species should be further developed. Discrepancies between observed and predicted activities for benthic species would be better resolved by incorporation of a well-defined microbial loop in the model.

This study did not consider ecosystem shifts (e.g. changes in species biomass and the knock-on effects) through time. However, if a model contamination study for an area covers an extensive period of time, then changes in the ecosystem which could affect contaminant concentration in the ecology should also be modelled in EwE. The Sellafield ^{14}C model and observed ^{14}C activities show that the ^{14}C activity for a functional group/species is dependent on the trophic level it feeds upon. Most ecosystems, in general, and the Irish Sea specifically, have undergone significant changes over the past century due to changes in the fishing/hunting pressures and climate, which result in species changing their foraging behaviour and the prey they feed on. This would affect the ^{14}C activity of a species and, if the contaminant was subject to bioaccumulation, this could lead to additional model complexities. Future work should consider this and, for ^{14}C, seek to address changes in ecosystem uptake due to seasonal variation in primary productivity.

6.4 Conclusions

This study modelled the ecosystem uptake and ecological fate of Sellafield ^{14}C discharged to the UK marine environment using the EwE software. Limitations in model advection to disperse ^{14}C through the marine environment meant that the specific ^{14}C activities predicted for some areas, such as the West of Scotland, did not compare well with observed activities. Further measurements of DIC ^{14}C activities, such as the Solway Firth where the model predicts an accumulation of Sellafield ^{14}C, would reduce uncertainty in dispersion patterns. The advantages of the EwE approach were illustrated in capturing observed trends in ^{14}C activities for species at specific locations and through time. In addition, the model data aids understanding of ^{14}C transfer processes through the food-web. ^{14}C does not bio-accumulate, although higher activities have been observed at higher trophic levels. The Sellafield model illustrates that changes in environmental ^{14}C activities will directly and immediately impact species activity at lower trophic levels, whereas higher trophic level species' ^{14}C activities are integrated over time. Therefore, species ^{14}C activity will

be strongly affected by the trophic level from which it feeds. The effectiveness of EwE for modelling the ecological fate of contaminants in the environment has been underrepresented despite the wide use of the EwE approach to ecosystem modelling. Recent developments in the software were utilised in this study. Further refinements, such as coupling this approach with better resolved contaminant dispersion, could be used to help address the ecological fate of a wide range of contaminants including radionuclides.

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Chapter 7
Project Conclusions

The preceding chapters discussed a number of studies which were undertaken to achieve the following project aims:

1) Determine the contemporary UK ^{14}C marine background to identify any ^{14}C enrichment as a result of Sellafield activities.
2) Develop a mechanistic understanding of uptake, transport and accumulation of ^{14}C in the inorganic component of intertidal sediments on the British west coast, addressing both particle and solution transport of inorganic ^{14}C.
3) Examine the transfer and extent of ^{14}C incorporation into near-source biotic and abiotic ecosystem components of the Irish Sea.
4) Examine ^{14}C transport to sites remote from Sellafield (West of Scotland) and the extent of ^{14}C incorporation into biotic and abiotic ecosystem components.
5) Investigate the trophic transfer of ^{14}C in the marine food web in relation to spatial and temporal changes in ambient ^{14}C activity.
6) Model the ecosystem uptake and trophic transfer of ^{14}C in the UK marine environment.

The significant conclusions of the entire project are listed below with notes on potential areas for future work.

- ^{14}C activities of whole mussel shells at sites close to Sellafield have varied in response to the average Sellafield ^{14}C discharge activity over the preceding 5 years.

- There has been a general increase in the ^{14}C activities of fine intertidal inorganic sediment in the north-east Irish Sea which has occurred as enriched whole shells have been broken down and evidence was found for the transport of this material to other sites.

- Enriched ^{14}C activities were detected in whole shells and shell fragments at intertidal sites remote from Sellafield in the west of Scotland showing long distance transport of dissolved ^{14}C.

- The differences in ^{14}C activities in whole shells of different species indicate that species ecology is important in determining the ^{14}C activity present in the shell.

- As whole shells erode there will be a continuing trend of increasing ^{14}C activities at sites in the north-east Irish Sea and this will be replicated in the west of Scotland, resulting in an increasing ^{14}C inventory in intertidal inorganic sediments.

- ^{14}C activities of water, sediment and organisms in the Irish Sea and west of Scotland marine environments were enriched and highly variable, although there is a general decline in ^{14}C activities with distance from source (Sellafield) as discharged ^{14}C is diluted within the marine carbon pools.

- A clear pathway exists of Sellafield-derived ^{14}C uptake by marine primary producers from the dissolved inorganic carbon pool, subsequent transfer to other marine organisms and deposition of enriched organic matter which re-enters the food-web, resulting in enriched ^{14}C activities at all trophic levels.

- Highly variable ^{14}C activities were observed in Irish Sea west basin (station WB) biota with some relatively high activities in benthic organisms which may be a result of the western Irish Sea gyre causing an accumulation of ^{14}C at depth

- Sediment ^{14}C activities at all sites were typically depleted relative to benthic organisms which is likely due to intensive mixing of surface sediments to depth via bioturbation and, in addition, rapid scavenging of ^{14}C enriched labile organic matter from the surface sediments.

- ^{14}C activities of fish species from different areas, i.e. Irish Sea east basin, west basin and west of Scotland, were typically distinct, although, migratory species were found to have different activities from other fish species in similar areas.

- Calculated dose rates (2.05 μSv) from the observed ^{14}C activities in fish and shellfish species for critical consumers of seafood were negligible when compared to the annual UK dose limit (1000 μSv) to members of the public from all man-made sources of radiation.

- Marine mammal ^{14}C activities correlated significantly with distance of stranding from Sellafield and Sellafield ^{14}C discharge activities prior to stranding.

- West of Scotland marine mammal ^{14}C activities correlated significantly with the total discharges made between 12 and 36 months prior to stranding indicating the transport time for ^{14}C to reach the west of Scotland environment.

- Data for harbour porpoise ^{14}C activities suggest this species has a high foraging fidelity and that the sampled west of Scotland animals did not forage in the Irish Sea.

- A novel approach to tracing ^{14}C in the environment was undertaken by developing an Ecopath with Ecosim (EwE) contaminant tracing model for the Irish Sea and West of Scotland environments.

- The observed trends in ^{14}C activities between different species, spatially and temporally, were predicted by the EwE model.

- Model data illustrated the previously hypothesised time-integration of Sellafield-derived ^{14}C in species at higher trophic levels, whereas ^{14}C activities of species at lower trophic levels respond quickly to changes in ambient ^{14}C activities.

Future work should consider the apparent increasing ^{14}C inventory of intertidal inorganic sediments in the Irish Sea and if this is being replicated at sites far from Sellafield, i.e. the west of Scotland. Any dissolution of this material will re-mobilise Sellafield-derived ^{14}C providing a secondary source to the marine environment. The ^{14}C activities presented in Chapter 2 were for sediments at specific points on the intertidal zone. To reduce uncertainty, ^{14}C activities should be analysed for multiple locations at each site for any future study.

Similarly, the exchange of ^{14}C between the food-web and marine organic sediments should be investigated including the ^{14}C activities of different organic carbon compounds and the role of microbes in recirculating ^{14}C (the microbial loop). Some additional measurements are being undertaken on sediments sampled during this project, as part of an ongoing study, and include ^{14}C activities in specific organic carbon compounds in marine sediments.

Analyses of sediment characteristics, such as grain size, porosity and permeability, have also been conducted and will be compared to radionuclide distribution downcore. These studies could improve our understanding of the observed differences in ^{14}C activities between benthic organisms and surface organic sediments and the long-term burial of ^{14}C in marine sediments. Additional future research could include plankton and sediment traps at multiple depths at various study sites. Data gathered from this type of study could significantly aid understanding of the temporal and spatial dispersion and biological uptake of ^{14}C. It could also provide additional information on the deposition and sedimentation of ^{14}C enriched organic matter.

The variation in ^{14}C activities down the water column was not specifically addressed in this project and could help understanding the variation in activities observed at, for example, the Irish Sea west basin. In co-ordination with phytoplankton and sediment trap studies, future work should consider ^{14}C measurements of seawater biogeochemical fractions, particularly DIC, down the water column. This would also aid modelling studies of ^{14}C dispersion.

The study examining the transfer of ^{14}C to resident apex predators was limited to harbour porpoises in the Irish Sea and other predators, such as seal, shark and seabird species, should be studied where possible. Variation in diet at these higher trophic levels is expected to be highly significant to individual ^{14}C activity and further work could address this and, also, reduce uncertainty of the effect time integration has on ^{14}C activities.

^{14}C measurements in this project were on soft tissues, typically muscle, and other tissue types should be considered in any future studies. Although bioaccumulation of ^{14}C would not be expected in any specific tissue type, the tissue turnover rate may significantly affect ^{14}C activities due to changes in ^{14}C integration. The biological half-life for ^{14}C in humans is 40 days but as it will be closely linked to the metabolic rate of an individual organism it could also vary been species and further analysis of this is required. Variable ^{14}C biological half-lives and ^{14}C activities between different tissue types would impact any dose assessments on the biota.

Dose assessments were made for humans based on the consumption of seafood enriched in ^{14}C as per the activities found. However, these studies did not include a dose assessment for the organisms analysed. None of the presented ^{14}C activities are considered to provide

a significant radiation dose to the organisms as indicated by preliminary results of a dose risk assessment. However, ^{14}C is only one of several radionuclides which have been historically discharged to the UK marine environment and a complete assessment study should be conducted which includes the data presented in this project in addition to other known radionuclide activities.

Seasonal variability in primary productivity will affect ^{14}C uptake into the marine ecosystem and the dispersion of ^{14}C in the marine environment. This should be the focus of further modelling studies which could include how climate change influences on primary productivity will affect ecosystem uptake of Sellafield-derived ^{14}C. These factors can be introduced using EwE.

The modelling approach utilised in Chapter 6 was a novel way of exploring how a radionuclide is transferred through an ecosystem and other studies of this nature should consider this approach. EwE allows the specific ecological fate of a contaminant to be examined down to the species level but within the wider context of how the contaminant is taken up by an ecosystem and transferred through the food-web.

Model results highlighted the potential for accumulation of ^{14}C in areas due to prevailing currents, although, the extent of accumulation did appear to be over-predicted. One area which was not considered during the analytical stages of this project, but should be in future studies, was the south-east Irish Sea. Seasonal southerly currents are known to exist which may result in some southward dispersion of Sellafield marine discharges.

The over-prediction of ^{14}C accumulation in some areas also revealed limitations of the model. Although the model predicted temporal trends in ^{14}C activity relatively well, the predicted spatial distribution of ^{14}C beyond the eastern Irish Sea did not agree well with observations. Observed activities in this project were typically for a specific location and at a single point of time, therefore, there is a large degree of uncertainty when comparing these with model results which are averaged spatially and temporally. However, it is likely that the dispersion of ^{14}C will be better resolved by a three-dimensional contaminant transport model. Spatially defined ^{14}C activities predicted by a transport model could be input to EwE and it is advised that any modelling work following this study should take this approach.

Appendix 1. Supplementary Tables for Chapter 3

Table A.1. Summary of benthic and planktonic species obtained at stations EB2 and WB, detailing the average species size (fish only) and size range (mm); the number of individuals analysed, and the gross specific ^{14}C activities (Bq kg^{-1} C ± 1σ) for each species.

Species	Common name	Station EB2 biota			Station WB biota		
		Ave. fish size [range] (mm)	No. analysed	^{14}C activity (Bq kg^{-1} C)	Ave. fish size [range] (mm)	No. analysed	^{14}C activity (Bq kg^{-1} C)
80-270 µm fraction	Phyto-plankton	-	net sample	520 ± 3	-	net sample	242 ± 1
>270 µm fraction	Zoo-plankton	-	net sample	458 ± 2	-	net sample	254 ± 1
Alcyonium digitatum	Soft coral	-	colony fragment	492 ± 2	-	-	-
Urticina felina	Dahlia anemone	-	1	542 ± 3	-	-	-
Polychaeta (various sp.)	Segmented worms	-	7	766 ± 4	-	8	318 ± 1
Maxmuelleria lankesteri	Green spoon worm	-	1	953 ± 4	-	-	-
Pagurus bernhardus (×3) *Goneplax rhomboides* (×5)	Hermit crab (3), angular crab (5)	-	8	658 ± 3	-	-	-
EB2 *Asterias rubens* (×1) *Astropecten irregularis* (×2) WB *Asteroidea spp.* (×4)	Starfish	-	3	718 ± 4	-	4	737 ± 3
Pleuronectes platessa	Plaice	180	1	673 ± 3	-	-	-
Limanda limanda	Dab (sample 1)	110 [80−130]	5	748 ± 4	110 [90−150]	5	831 ± 4
	Dab (sample 2)		5	1012 ± 5		5	752 ± 3
Aphrodita aculeata	Sea mouse	-	-	-	-	1	989 ± 4
Callianassa subterranea	Mud shrimp (sample 1)	-	-	-	-	5	266 ± 1
	Mud shrimp (sample 2)	-	-	-	-	5	270 ± 1
Echinocardium cordatum	Heart urchin	-	-	-	-	4	285 ± 1
Calocaris macandreae	Shrimp (sample 1)	-	-	-	-	5	300 ± 1
	Shrimp (sample 2)	-	-	-	-	5	308 ± 1
Nephrops norvegicus	*Nephrops* (sample 1)	-	-	-	-	5	299 ± 1
	Nephrops (sample 2)	-	-	-	-	5	296 ± 1
Callionymus lyra	Dragonet	-	-	-	120 [100-140]	3	737 ± 3

Table A.2. Summary of the species obtained during the fish/ scallop stock surveys conducted by AFBI-NI, detailing the average (fish only) species size and size range (mm); the number of individuals analysed for ^{14}C and the gross specific ^{14}C activities (Bq kg^{-1} C ± 1σ) for each species.

Station	Species	Common name	Ave. fish size [size range] (mm)	Number analysed	^{14}C specific activity (Bq kg^{-1} C)
86	*Gadus morhua*	Cod	270 [250−300]	3	275 ± 1
208	*Melanogrammus aeglefinus*	Haddock (sample 1)	200 [160−220]	5	267 ± 1
		Haddock (sample 2)		5	267 ± 1
208	*Clupea harengus*	Herring (sample 1)	200 [150−240]	5	257 ± 1
		Herring (sample 2)		5	262 ± 1
208	*Scomber scombrus*	Mackerel	230 [190−280]	5	249 ± 1
208	*Nephrops norvegicus*	Norway lobster (sample 1)	-	5	276 ± 1
		Norway lobster (sample 2)	-	5	278 ± 1
257	*Nephrops norvegicus*	Norway lobster (sample 1)	-	5	549 ± 2
		Norway lobster (sample 2)	-	5	554 ± 2
259	*Melanogrammus aeglefinus*	Haddock (sample 1)	240 [210−270]	3	469 ± 2
		Haddock (sample 2)		3	464 ± 2
242	*Melanogrammus aeglefinus*	Haddock	290	1	322 ± 1
242	*Ammodytes tobianus*	Sandeel	240 [230−250]	2	313 ± 1
242	*Clupea harengus*	Herring	200 [190−210]	5	274 ± 1
242	*Scomber scombrus*	Mackerel (sample 1)	230 [220−240]	3	289 ± 1
		Mackerel (sample 2)		3	310 ± 1
342	*Ammodytes tobianus*	Sandeel	255 [250-260]	5	315 ± 1
342	*Melanogrammus aeglefinus*	Haddock	230 [210−260]	5	293 ± 1
245	*Gadus morhua*	Cod	270 [250−290]	5	285 ± 1
Area G	*Pecten maximus*	King scallop	-	5	287 ± 1
Area H	*Pecten maximus*	King scallop	-	5	285 ± 1

Appendix 2. Supplementary Tables for Chapter 4

Table A.3. Summary of benthic and planktonic species obtained at stations NC and FoL, detailing the number of individuals analysed for ^{14}C, and the gross specific ^{14}C activities (Bq kg^{-1} C ± 1σ) for each species.

Species	Sample name	Station NC biota		Station FoL biota	
		No. analysed	^{14}C activity (Bq kg^{-1} C)	No. analysed	^{14}C activity (Bq kg^{-1} C)
Plankton 80-270 µm fraction	Phytoplankton	net sample	280 ± 2	net sample	241 ± 1
>270 µm fraction	Zooplankton	net sample	283 ± 2	net sample	227 ± 1
Cerastoderma edule	Cockle (sample 1)	8	316 ± 2	-	-
	Cockle (sample 2)	8	314 ± 2	-	-
Funiculina quadrangularis	Sea Pen	-	-	colony fragment	267 ± 2
Echinus esculentus	Edible Sea Urchin	-	-	2	266 ± 2
Echinocardium cordatum	Heart Urchin	12	307 ± 2	1	261 ± 1
Holothurian sp.	Sea Cucumber	-	-	2	274 ± 2
Nemertea sp.	Ribbon Worms	-	-	5	282 ± 2
Maldanidae sp., Nephtys sp., Chaetopterus variopedatus	Polychaete Worms	8	320 ± 1	5	271 ± 1
Aphrodita aculeata	Spoon Worm	-	-	2	277 ± 2
Ophiocomina nigra, Ophiothrix fragilis, Ophiura albida	Black brittlestar	-	-	4	292 ± 2
	Common brittlestar	-	-	5	289 ± 2
	Serpent's table brittlestar	-	-	7	278 ± 1
	Mixed brittlestar sp.	10	319 ± 2	-	-
Calocaris macandreae	Calocaris shrimp (sample 1)	5	298 ± 2	-	-
	Calocaris shrimp (sample 2)	5	299 ± 2	-	-
Callianassa subterranea	Mud shrimp	-	-	2	275 ± 2
Jaxea nocturna	Jaxea Shrimp	-	-	1	269 ± 2
Pagurus prideaux, Pagurus bernhardus	Hermit crab (sample 1)	4	296 ± 2	3	269 ± 2
	Hermit crab (sample 2)	4	295 ± 2	-	-

Species	Sample name	Station NC biota		Station FoL biota	
		No. analysed	^{14}C activity (Bq kg^{-1} C)	No. analysed	^{14}C activity (Bq kg^{-1} C)
Goneplax rhomboides, Atelecyclus rotundatus, Inachus sp.	Circular crab	-	-	2	268 ± 2
	Spider crab	-	-	3	269 ± 2
	Mixed crab sp. (sample 1)	5	299 ± 2	-	-
	Mixed crab sp. (sample 2)	5	300 ± 2	-	-
Buccinum undatum	Common Whelk	-	-	2	279 ± 2
Aphrodita aculeata	Sea mouse (sample 1)	4	316 ± 2	1	278 ± 2
	Sea mouse (sample 2)	4	323 ± 1	-	-
Asterias rubens, Crossaster papposus, Luidia sarsii, Asteroidea sp.	Mixed starfish (sample 1)	4	327 ± 2	3	273 ± 2
	Mixed starfish (sample 2)	4	316 ± 1	-	-
Munida rugosa	Squat lobster	-	-	2	274 ± 2
Nephrops norvegicus	Nephrops (sample 1)	5	315 ± 1	5	275 ± 2
	Nephrops (sample 2)	5	312 ± 1	5	268 ± 2
Limanda limanda	Dab (sample 1)	3	278 ± 2	-	-
	Dab (sample 2)	3	321 ± 2	-	-
Buglossidium luteum	Sole (sample 1)	5	328 ± 2	-	-
	Sole (sample 2)	5	321 ± 2	-	-
Lepidorhombus whiffiagonis	Megrim	-	-	1	275 ± 2
Callionymus lyra	Dragonet (sample 1)	3	303 ± 2	-	-
	Dragonet (sample 2)	3	296 ± 2	-	-
Molva molva	Ling	2	302 ± 2	-	-
Merlangius merlangus	Whiting	3	413 ± 2	-	-

Table A.4. Summary of the species obtained during the fish/ scallop stock surveys conducted by Marine Scotland Science and AFBI Northern Ireland, detailing the number of individuals analysed for ^{14}C and the gross specific ^{14}C activities (Bq kg^{-1} C ± 1σ) for each species.

Station	**Species**	**Common name**	**Number analysed**	**^{14}C specific activity (Bq kg^{-1} C)**
H443	*Melanogrammus aeglefinus*	Haddock (sample 1)	4	297 ± 2
		Haddock (sample 2)	4	296 ± 2
H443	*Clupea harengus*	Herring (sample 1)	6	284 ± 2
		Herring (sample 2)	6	282 ± 2
H443	*Merlangius merlangus*	Whiting	4	288 ± 2
H443	*Cancer pagurus*	Edible crab	1	292 ± 2
H444	*Cancer pagurus*	Edible crab	1	304 ± 2
H445	*Cancer pagurus*	Edible crab	2	288 ± 2
H445	*Melanogrammus aeglefinus*	Haddock	4	286 ± 2
H451	*Lophius piscatorius*	Monkfish	4	250 ± 1
Area A	*Pecten maximus*	King scallop	5	249 ± 1
Area D	*Pecten maximus*	King scallop	5	282 ± 2

Appendix 3. Supplementary Tables for Chapter 6

Table A.5. Sellafield model functional groups and balanced input parameters; biomass, production/biomass (P/B), consumption/biomass (Q/B), ecotrophic efficiency (EE), production/consumption (P/Q) and unassimilated consumption. Values used before balancing are shown in brackets, where applicable.

Group name	Biomass (t/km^2)	P/B (/year)	Q/B (/year)	EE	P/Q	Unassimilated consumption
Bottlenose Dolphin	0.0016	0.2	8.67			0.2
Harbour Porpoise	0.0105	0.2	8.67			0.2
Minke Whale	0.0893	0.02	10			0.2
Common Seal	0.0005	0.1	14.55			0.2
Grey Seal	0.004	0.1	14.55			0.2
Seabirds	0.0511	1.075	82.664			0.2
Large Sharks	0.115	0.318	3.18			0.2
Small Sharks	0.288	0.972	9.72			0.2
Basking Sharks	0.0014	0.07	3.7			0.2
Skates and Rays	0.103	1.6	16			0.2
Cod	0.6253	1.3891	4.7051			0.2
Haddock	0.2711	2.4751	8.5356			0.2
Plaice	0.3425	1.3522	5.6234			0.2
Whiting	0.55 (0.507)	0.842	2.97			0.2
Sole	0.16	0.863	2.58			0.2
Monkfish	(0.125)	(1.246)	1.989	0.95	0.2	0.2
Dab	(0.07)	(2.394)	3.042	0.95	0.2	0.2
Other Flatfish	(0.2404)	(2.1757)	3.8572	0.95	0.2	0.2
Dragonets	0.229	1.54	5.154			0.2
Mackerel	1.623	0.414	4.4 (1.73)			0.2
Ling	0.076	1.315	3.089			0.2
Other Demersals	2.4158	1.5384	4.5888			0.2
Herring	1.2131	1.154 (0.727)	6.516			0.2
Other Small Pelagic Planktivorous Fish	2.4262	0.727	6.516			0.2
Sandeels	1.3	1.53	5.016			0.2
Epifaunal Macrobenthos	13	1.661			0.2	0.2
Epifaunal Mesobenthos	8.999 (8.975)	2.062			0.22	0.2
Infaunal Macrobenthos	8.007	2.695			0.2	0.2
Infaunal Mesobenthos	24.773	2.552			0.22	0.2
Infauna (Polychaete)	22.726	3.683			0.3	0.2
Lobster and Large Crabs	0.11 (0.098)	0.783	5.22			0.2

Group name	Biomass (t/km^2)	P/B (/year)	Q/B (/year)	EE	P/Q	Unassimilated consumption
Nephrops	(0.35)	0.73	4.867	0.95		0.2
Cephalopods	0.25	1.981	15			0.2
Prawns and Shrimp	4.925 (4.847)	0.959	6.393			0.2
Sessile Epifauna	7.5	2.066			0.2	0.2
Meiofauna	6.314	18.45			0.3	0.2
Zooplankton	(48.475)	15.2855		0.95	0.3	0.2
Seaweed	75	60				
Microflora	3.92	587				
Phytoplankton	13.83	70.14				
Particulate Organic Matter	50					
Dissolved Organic Matter	50					
Discards	0.309					

Table A.6. Sellafield model diet matrix with values used pre- balancing in parentheses.

Prey \ predator	Bottlenose Dolphin	Harbour Porpoise	Minke Whale	Common Seal	Grey Seal	Seabirds
Bottlenose Dolphin	0	0	0	0	0	0
Harbour Porpoise	0	0	0	0	0	0
Minke Whale	0	0	0	0	0	0
Common Seal	0	0	0	0	0	0
Grey Seal	0	0	0	0	0	0
Seabirds	0	0	0	0	0	0.0100
Large Sharks	0	0	0	0	0	0
Small Sharks	0.1000	0	0	0.0050	0.0100	0.0010
Basking Sharks	0	0	0	0	0	0
Skates and Rays	0.1000	0	0	0.0790	0.0300	0.0040
Cod	0	0.0059	0	0	0	0.0410
Haddock	0.0593	0.0135	0	0	0	0.0160
Plaice	0.0027	0	0	0.0032	0	0.0050
Whiting	0.0200	0.2130	0	0.0350	0.0300	0.0240
Sole	0.0010	0	0	0.0200	0.0200	0.0070
Monkfish	0	0	0	0	0	0.0010
Dab	0.0044	0.0066	0	0.0338	0.0182	0.0073
Other Flatfish	0.0186	0.0304	0	0.1025	0.0292	0.0257
Dragonets	0	0	0	0.0371	0.0055	0.0120
Mackerel	0.0126	0.0149	0.2500 (0.4000)	0	0.0950	0.0390
Ling	0.1805	0	0	0.1000	0.0900	0.0130
Other Demersals	0.4615	0.4122	0	0.3873	0.4998	0.1602
Herring	0.0089	0.0563	0.2600 (0.1300)	0.0247	0.0290	0.0020
Other Planktivorous Fish	0.0177	0.1126	0.2800 (0.2600)	0.0493	0.0579	0.0040
Sandeels	0	0.1000	0.0050	0.1038	0.0160	0.1481
Epifaunal Macrobenthos	0	0	0	0	0	0.0521
Epifaunal Mesobenthos	0	0	0	0	0	0.0521
Infaunal Macrobenthos	0	0	0	0	0	0
Infaunal Mesobenthos	0	0	0	0	0	0
Infauna (Polychaete)	0	0	0	0	0	0.1051
Lobster and Large Crabs	0	0	0	0	0.0150	0.0020
Nephrops	0	0	0	0	0.0150	0
Cephalopods	0.0129	0.0343	0.0900	0.0191	0.0395	0
Prawns and Shrimp	0	0	0.1000	0	0	0.1682
Sessile Epifauna	0	0	0	0	0	0
Meiofauna	0	0	0	0	0	0
Zooplankton	0	0	0.0150	0	0	0
Seaweed	0	0	0	0	0	0
Microflora	0	0	0	0	0	0
Phytoplankton	0	0	0	0	0	0
Particulate Organic Matter	0	0	0	0	0	0.0800 (0)
Dissolved Organic Matter	0	0	0	0	0	0
Discards	0	0	0	0	0	0.0200 (0.1000)

Prey \ predator	Large Sharks	Small Sharks	Basking Sharks	Skates and Rays	Cod	Haddock
Bottlenose Dolphin	0	0	0	0	0	0
Harbour Porpoise	0	0	0	0	0	0
Minke Whale	0	0	0	0	0	0
Common Seal	0	0	0	0	0	0
Grey Seal	0	0	0	0	0	0
Seabirds	0	0	0	0	0	0
Large Sharks	0	0	0	0	0	0
Small Sharks	0	0	0	0.0060	0	0
Basking Sharks	0	0	0	0	0	0
Skates and Rays	0	0	0	0.0030	0	0
Cod	0	0	0	0	0.0043	0
Haddock	0	0	0	0	0.0108	0.0074
Plaice	0	0	0	0	0	0
Whiting	0	0	0	0.0080	0.0168	0
Sole	0	0	0	0	0	0
Monkfish	0	0	0	0	0	0
Dab	0	0	0	0.0022	0.0021	0
Other Flatfish	0	0.0940	0	0.0018	0.0036	0
Dragonets	0	0	0	0.0180	0.0057	0.0015
Mackerel	0	0	0	0.0060	0.0206	0.0008
Ling	0	0	0	0	0	0
Other Demersals	0	0.2480	0	0.0640	0.0243	0
Herring	0	0.0513	0	0.0027	0.0036	0
Other Planktivorous Fish	0	0.1026	0	0.0053	0.0072	0
Sandeels	0	0.1340	0	0.0040	0.0240	0.0090
Epifaunal Macrobenthos	0.6650	0.3140	0	0.2510	0.3780	0.1206
Epifaunal Mesobenthos	0.0150	0	0	0.0310	0.0449	0.0839
Infaunal Macrobenthos	0.2000	0.0010	0	0	0	0.0129
Infaunal Mesobenthos	0	0.0010	0	0	0	0.0129
Infauna (Polychaete)	0.0350	0	0	0.0210	0.0672	0.0676
Lobster and Large Crabs	0	0.0400	0	0	0	0
Nephrops	0	0	0	0.0010	0.0280	0
Cephalopods	0.0850	0	0	0.0070	0.0023	0.0015
Prawns and Shrimp	0	0.0010	0	0.4530	0.0529	0.0482
Sessile Epifauna	0	0	0	0	0	0.0008
Meiofauna	0	0	0	0	0	0
Zooplankton	0	0.0130	1.0000	0.1080	0.2823	0.4837
Seaweed	0	0	0	0	0	0.0008
Microflora	0	0	0	0	0	0
Phytoplankton	0	0	0	0	0.0215	0.1484
Particulate Organic Matter	0	0	0	0.0070	0	0
Dissolved Organic Matter	0	0	0	0	0	0
Discards	0	0	0	0	0	0

Prey \ predator	Plaice	Whiting	Sole	Monkfish	Dab	Other flatfish
Bottlenose Dolphin	0	0	0	0	0	0
Harbour Porpoise	0	0	0	0	0	0
Minke Whale	0	0	0	0	0	0
Common Seal	0	0	0	0	0	0
Grey Seal	0	0	0	0	0	0
Seabirds	0	0	0	0	0	0
Large Sharks	0	0	0	0	0	0
Small Sharks	0	0	0	0	0	0
Basking Sharks	0	0	0	0	0	0
Skates and Rays	0	0	0	0	0	0
Cod	0	0.0200	0	0.0110	0.0020	0.0411
Haddock	0	0.0200	0	0.0055	0.0020	0.0411
Plaice	0.0042	0	0	0.1044	0	0
Whiting	0	0.0100	0	0.0110	0.0020	0.0002
Sole	0	0.0100	0	0.0440	0	0
Monkfish	0	0.0500	0	0	0.1000	0.0112
Dab	0	0.0219	0	0.0778	0.0015	0.0002
Other Flatfish	0	0.0581	0	0.1343	0.0025	0.0003
Dragonets	0.0056	0.0060	0	0.1055	0.0100 (0.1000)	0.0100 (0.0112)
Mackerel	0	0.0240	0	0.1363	0.0050	0.0006
Ling	0	0	0	0	0	0
Other Demersals	0.0056	0.1740	0	0.2000	0.2040 (0.2199)	0.1282
Herring	0	0.0480	0	0.0351	0.0127	0.0165
Other Planktivorous Fish	0	0.0959	0	0.0703	0.0253	0.0331
Sandeels	0.0112	0.1100	0	0.0110	0.0200	0.1064
Epifaunal Macrobenthos	0.0562	0.1160	0.1000	0.0110	0.1540	0.1110 (0.1381)
Epifaunal Mesobenthos	0.1404	0.0170	0.2500	0	0.0020	0.0095
Infaunal Macrobenthos	0.1404	0	0.2500	0	0	0.0093
Infaunal Mesobenthos	0.1050	0	0.1500	0	0	0
Infauna (Polychaete)	0.2277	0.0120	0.2500	0.0110	0.2200 (0.1140)	0.1200 (0.1336)
Lobster and Large Crabs	0	0	0	0.0077	0	0
Nephrops	0	0.0010	0	0.0033	0.0009	0.0001
Cephalopods	0	0.0160	0	0	0.0070	0.0380
Prawns and Shrimp	0.0624	0.0850	0	0.0209	0.1070	0.1235
Sessile Epifauna	0	0	0	0	0.0004	0
Meiofauna	0	0	0	0	0	0
Zooplankton	0.1997	0.1050	0	0	0.1220	0.1993
Seaweed	0	0	0	0	0	0
Microflora	0	0	0	0	0	0
Phytoplankton	0.0416	0	0	0	0	0
Particulate Organic Matter	0	0	0	0	0	0
Dissolved Organic Matter	0	0	0	0	0	0
Discards	0	0	0	0	0	0

Prey \ predator	Dragonet	Mackerel	Ling	Other Demersals	Herring	Other Planktiv-orous Fish
Bottlenose Dolphin	0	0	0	0	0	0
Harbour Porpoise	0	0	0	0	0	0
Minke Whale	0	0	0	0	0	0
Common Seal	0	0	0	0	0	0
Grey Seal	0	0	0	0	0	0
Seabirds	0	0	0	0	0	0
Large Sharks	0	0	0	0	0	0
Small Sharks	0	0	0	0	0	0
Basking Sharks	0	0	0	0	0	0
Skates and Rays	0	0.0010	0	0	0	0
Cod	0	0	0	0.0040	0	0
Haddock	0	0	0	0.0004	0	0
Plaice	0	0	0	0	0	0
Whiting	0	0	0	0.0019	0	0
Sole	0	0	0	0.0031	0	0
Monkfish	0	0	0	0	0	0
Dab	0	0	0	0.0027	0	0
Other Flatfish	0	0	0	0.0019	0	0
Dragonets	0	0	0	0.0098	0	0
Mackerel	0	0.0007	0	0.0098	0	0
Ling	0	0	0	0	0	0
Other Demersals	0	0.0010	0	0.0325	0.0100	0.0100
Herring	0	0.0030	0	0.0095	0.0007	0.0007
Other Planktivorous Fish	0	0.0060	0	0.0190	0.0013	0.0013
Sandeels	0	0	0	0.0085	0	0
Epifaunal Macrobenthos	0.6420	0.0280	0.5000	0.0914	0.0280	0.0280
Epifaunal Mesobenthos	0	0.0090	0	0.0781	0.0060	0.0060
Infaunal Macrobenthos	0	0	0	0.0006	0	0
Infaunal Mesobenthos	0	0	0	0.0003	0	0
Infauna (Polychaete)	0.2860	0.0007	0	0.0207	0.0020	0.0020
Lobster and Large Crabs	0	0	0	0	0	0
Nephrops	0	0	0.0500	0.0018	0	0
Cephalopods	0	0.0010	0	0.0033	0.0005	0.0005
Prawns and Shrimp	0	0	0.4500	0.1538	0.0060	0.0060
Sessile Epifauna	0	0	0	0	0	0
Meiofauna	0	0	0	0	0	0
Zooplankton	0.0720	0.9373	0	0.4772	0.9455	0.9455
Seaweed	0	0	0	0	0	0
Microflora	0	0	0	0	0	0
Phytoplankton	0	0.0003	0	0	0	0
Particulate Organic Matter	0	0.0120	0	0.0697	0	0
Dissolved Organic Matter	0	0	0	0	0	0
Discards	0	0	0	0	0	0

Prey \ predator	Sandeels	Epifaunal Macro-benthos	Epifaunal Meso-benthos	Infaunal Macro-benthos	Infaunal Meso-benthos	Infauna Polychaete
Bottlenose Dolphin	0	0	0	0	0	0
Harbour Porpoise	0	0	0	0	0	0
Minke Whale	0	0	0	0	0	0
Common Seal	0	0	0	0	0	0
Grey Seal	0	0	0	0	0	0
Seabirds	0	0	0	0	0	0
Large Sharks	0	0	0	0	0	0
Small Sharks	0	0	0	0	0	0
Basking Sharks	0	0	0	0	0	0
Skates and Rays	0	0	0	0	0	0
Cod	0	0	0	0	0	0
Haddock	0	0	0	0	0	0
Plaice	0	0	0	0	0	0
Whiting	0	0	0	0	0	0
Sole	0	0	0	0	0	0
Monkfish	0	0	0	0	0	0
Dab	0	0	0	0	0	0
Other Flatfish	0	0	0	0	0	0
Dragonets	0	0	0	0	0	0
Mackerel	0	0	0	0	0	0
Ling	0	0	0	0	0	0
Other Demersals	0	0	0	0	0	0
Herring	0	0	0	0	0	0
Other Planktivorous Fish	0	0	0	0	0	0
Sandeels	0	0	0	0	0	0
Epifaunal Macrobenthos	0	0.0270	0	0.0220	0	0
Epifaunal Mesobenthos	0	0.1040	0.0100	0.0220	0.0059	0
Infaunal Macrobenthos	0	0.1760	0	0.0120	0	0
Infaunal Mesobenthos	0	0.1770	0.3200	0.1330	0.0059	0
Infauna (Polychaete)	0	0.1780	0.3200	0.1330	0.0554	0
Lobster and Large Crabs	0	0	0	0	0	0
Nephrops	0	0	0	0	0	0
Cephalopods	0	0	0	0	0	0
Prawns and Shrimp	0	0	0	0	0	0
Sessile Epifauna	0	0.0060	0	0	0.0495	0
Meiofauna	0	0	0.3000	0.1120	0.1484	0
Zooplankton	0.6000	0.0760	0	0.1640	0.0425	0
Seaweed	0	0.0390	0.0400	0	0	0
Microflora	0	0.0370	0.0100	0.0010	0.1098	0.3300
Phytoplankton	0.1000	0.0190	0	0.2710	0.1098	0
Particulate Organic Matter	0.3000	0.1420 (0.1210)	0	0.0650	0.1650 (0.1098)	0.3400
Dissolved Organic Matter	0	0.0190	0	0.0650	0.3076	0.3300
Discards	0	0 (0.0210)	0	0	0 (0.0554)	0

Prey \ predator	Lobster and Large Crabs	Nephrops	Cephalo-pods	Prawns and Shrimp	Sessile Epifauna	Meiofauna	Zoo-plankton
Bottlenose Dolphin	0	0	0	0	0	0	0
Harbour Porpoise	0	0	0	0	0	0	0
Minke Whale	0	0	0	0	0	0	0
Common Seal	0	0	0	0	0	0	0
Grey Seal	0	0	0	0	0	0	0
Seabirds	0	0	0	0	0	0	0
Large Sharks	0	0	0	0	0	0	0
Small Sharks	0	0	0	0	0	0	0
Basking Sharks	0	0	0	0	0	0	0
Skates and Rays	0	0	0	0	0	0	0
Cod	0	0	0.0098	0	0	0	0
Haddock	0	0	0.0098	0	0	0	0
Plaice	0	0	0.0098	0	0	0	0
Whiting	0	0	0.0010	0	0	0	0
Sole	0	0	0.0098	0	0	0	0
Monkfish	0	0	0	0	0	0	0
Dab	0	0	0.0072	0	0	0	0
Other Flatfish	0	0	0.0026	0	0	0	0
Dragonets	0	0	0	0	0	0	0
Mackerel	0	0	0	0	0	0	0
Ling	0	0	0	0	0	0	0
Other Demersals	0	0.0090	0.0029	0	0	0	0
Herring	0	0	0.0003	0	0	0	0
Other Planktivorous Fish	0	0	0.0007	0	0	0	0
Sandeels	0	0	0.0010	0	0	0	0
Epifaunal Macrobenthos	0.0500	0.0700	0.0196	0	0	0	0
Epifaunal Mesobenthos	0.0500	0.0700	0.0196	0	0	0	0
Infaunal Macrobenthos	0.0500	0.0700	0.0196	0	0	0	0
Infaunal Mesobenthos	0.0500	0.0700	0.0196	0	0	0	0
Infauna (Polychaete)	0	0.0500	0.0098	0	0	0.0100	0
Lobster and Large Crabs	0.0300	0	0.0049	0	0	0	0
Nephrops	0	0	0.0010	0	0	0	0
Cephalopods	0	0	0.0010	0	0	0	0
Prawns and Shrimp	0.1700 (0.1500)	0	0.0098	0	0	0	0
Sessile Epifauna	0	0.1610	0	0	0	0	0
Meiofauna	0	0	0	0	0	0.0900	0
Zooplankton	0	0	0.6438	0.0900	0.2970	0	0.2000 (0.3017)
Seaweed	0	0	0	0	0	0	0
Microflora	0	0	0	0	0.1430	0.7000	0
Phytoplankton	0	0	0.1963	0.0800	0.1430	0	0.4590 (0.3565)
Particulate Organic Matter	0.6000 (0.6200)	0.4700 (0)	0	0.5200	0.1430	0.2000	0.1498
Dissolved Organic Matter	0	0	0	0.3100	0.2740	0	0.1920
Discards	0.0200 0	0.0300 (0.5000)	0	0	0	0	0